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RUBBER CHEMISTRY AND TECHNOLOGY

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ON THE DEGREE OF CRYSTALLINITY IN NATURAL RUBBER.

I. AN IMPROVED METHOD TO DETERMINE THE DEGREE OF CRYSTALLIZATION IN RUBBER *

J. M. GOPPEL

Introduction.—Generally speaking, high polymeric substances crystallize only partially because very long, entangled molecules are very unlikely to straighten out and to rearrange themselves into highly ordered regions. In the case of rubber, it is evident from x-ray diagrams that, whether rubber is crystallized by stretching or by freezing, part of it remains amorphous. Regarding the amounts of amorphous and crystallized rubber, until 1941 only a few estimates exist, in spite of the importance of the matter. Field¹ was the first investigator to publish, in an interesting paper, the results of quantitative measurements in this field of research by the use of x-ray methods.

Estimates of earlier data are in serious contradiction to Field's results. Parks² considered the stepwise variations in dv/dt and ds/dt , occurring at the stiffening point of amorphous rubberlike substances, v , s and t representing volume, specific heat and time. These variations are typical for a second-order transition point, and Parks pointed out that crystallized high polymers should not display such discontinuities. They are caused in general by the stopping of certain micro-Brownian motions which are no longer possible in crystallized substances. Frozen rubber still possesses a second-order transition point, and this fact, is according to Parks, due to partial crystallization of the rubber, leaving the greater part in the amorphous state. From the magnitude of the effect in the case of frozen and amorphous rubber, Parks concluded that there is only 20–30 per cent of crystalline rubber in frozen samples.

Another estimate was made by Smith and Saylor³. They measured the density of rubber samples, crystallized by stretching and by freezing, and estimated the degree of crystallization from a combination of these measurements with density figures derived from x-ray investigations. Thus in frozen and stretched samples of raw rubber, 30 and 45 per cent, respectively, of crystalline rubber hydrocarbon was found to be present, a comparatively low amount, in agreement with Parks's statement.

Field, measuring the amount of crystalline rubber in vulcanized samples, concludes on the contrary that very high percentages are present. According to his results, a degree of crystallization of 80 per cent would easily be reached. Even at higher temperatures (90° C) stretched rubber would be crystalline for about 60 per cent. In view of the lower estimates mentioned and of the extreme stiffening which would accompany such high degrees of crystallization,

* Reprinted from *Applied Scientific Research*, Vol. A1, No. 1, pages 3–26 (1947). The investigation was carried out by the author in his capacity as research assistant of the Delft University Fund (Delftsch Hoogeschoolfonds) and the Rubber Foundation. The investigation has been described in detail in the author's thesis at the Delft Technical University "Quantitative Röntgenografische Onderzoekingen aan Rubber," Delft, 1946.

Field's values were considered with some reserve, and it seemed desirable to have them checked. Investigation started in 1942, and resulted in values strongly diverging from Field's. As the contradiction remained, even after the technique of measuring was improved to a rather exact method of quantitative x-ray analysis, it may be of importance to report on the results obtained.

Quantitative x-ray analysis; Field's method.—Quantitative x-ray analysis has become a very important means to determine the composition of systems to which methods of normal chemical analysis cannot be applied; *e.g.*, when the components react chemically in the same way or when the difference between the constituents is of a physical nature. x-Ray measurements are likely to make possible a solution of the problem if the constituents are of different crystal structure, which is the case when the ratio of the crystalline and amorphous phases in partly crystallized rubber is to be determined. The analysis of rubber, carried out by Field, is based on the following facts:

1. Relation between the intensity of the diffracted radiation and the amount of diffracting substance, particularly between the intensity of the diffuse halo, characteristic of amorphous substances, and the thickness of an unstretched sample of rubber.

2. Decrease of intensity of the amorphous halo as crystallization increases, accompanied by the appearance of diffraction spots of increasing intensity.

The x-ray diffraction by amorphous rubber will first be considered. The diffraction pattern consists of a diffuse halo, the maximum intensity of which will be denoted by I_a^4 . I_a depends on the thickness of the rubber and the relation is represented with sufficient approximation by:

$$I_a(d) = cI_0td \exp(-\mu d) \quad (1)$$

if d = thickness of the sample, c = constant factor, I_0 = intensity of the primary beam, t = time of exposure, μ = extinction coefficient.

Next the intensity of the amorphous halo $I_{a,g}$, diffracted by a partly crystallized sample, is considered. Again approximately this intensity can be represented by:

$$I_{a,g} = cI_0d_a \exp(-\mu d_w) \quad (2)$$

if d_a = effective thickness of amorphous rubber, d_w = total thickness of the sample.

The amount of amorphous rubber is then, of course, given by:

$$A = \frac{d_a}{d_w} 100\% \quad (3)$$

Field first carried out measurements on the intensity I_a of the amorphous halo as a function of the thickness of unstretched rubber samples; the established relation was then used to obtain d_a values from $I_{a,g}$ measurements, d_a thus being determined by Equation (1). However, owing to the larger absorption caused by the actual thickness $d_w > d_a$, the intensity $I_{a,g}$ is lower than would be found in a completely amorphous sample of thickness d_a . Therefore d_a should be determined from (2), and the use of (1) can be shown to lead to erroneous results, due to which Field's values for the degree of crystallinity are up to 20 per cent too high.

One will have noticed that the total amount of x-rays, I_0t , falling on the sample during every exposure is assumed to be known. Now several authors

have emphasized the extreme difficulties involved in producing x-ray patterns in such a manner that the amount of radiation for every exposure is constant⁶. Therefore one should not bother about absolute values, but preferably measure ratios of intensities I_a and I_0 . This necessitates recording the intensity of the primary beam, and Nahmias⁶ has developed a fine method by simultaneously exposing the sample under investigation and an aluminum wire, serving as a carrier filament for the first sample. The intensity of the Al reflections is a measure of the intensity of the primary beam of x-rays. One might suggest that the primary beam itself, after being reduced by filters to suitable intensity, should perhaps be able to be used for the same purpose, and this is the way in which Field has tried to overcome difficulties arising from intensity variations in the radiation. The intensity of the spot, thus caused by the primary beam, may be given by:

$$I_s = kI_0 \exp(-\mu d_w) \quad (4)$$

where μ = absorption factor of the rubber sample, k = constant factor, depending on absorption in the filter, in air, distance from specimen to film, etc.

Using the ratio I/I_s instead of the absolute intensities, (1) and (2) are rid of the absorption factors $\exp(-\mu d)$ and become identical. Thus by using the primary beam itself as a reference intensity, no errors are involved when using (1) instead of (2) to calculate d_a , but this is a very risky way of eliminating the effect of intensity variations. The spectrum of an ordinary x-ray tube not only contains the characteristic Cu-K α radiation, but lower wave lengths also are present. Filtering the radiation now reduces especially the intensity of the higher wave lengths, the intensity of the hard radiation being hardly decreased. The control spot, obtained by weakening of the primary beam by absorption, is therefore principally due to lower wave lengths, the intensity of which depends on voltage fluctuations in quite another way from that of the intensity of the Cu-K α radiation. The control spot therefore represents no measure for the intensity of the characteristic radiation; producing the diffraction pattern, and using this spot as a reference for the other intensities, measured in the diagram, certainly does not simplify (1) and (2) in the way mentioned above. The absorption thus influences Field's results in two ways: first with respect to the determination of d_a and, secondly, with respect to the control of the intensity of the primary beam.

Finally another objection to the way in which Field linked up the results obtained on raw rubber with measurements of vulcanized samples may be raised. Field proceeded by measuring the intensity, I_r , of the diffraction spots caused by the crystalline rubber, and he associates the ratio, $I_r/I_{a,g}$, with the degree of crystallinity obtained in the way mentioned from intensity measurements on the diffuse halo. The relation thus established for raw rubber serves to interpret $I_r/I_{a,g}$ values in the case of vulcanized rubber. The x-ray absorption of vulcanized rubber depends strongly on the composition, and the mere influence of absorption on Field's results renders such an extrapolation unjustified.

Improved method to determine the degree of crystallization.—Preliminary measurements carried out in the x-ray department of the Delft Technical University were arranged in such a manner as to duplicate those of Field. Only the rate of stretching differed from that used by Field. The samples were stretched stepwise from 0–100, 100–200 per cent elongation, etc., because, in view of the work of Holt and Macpherson⁷, the rate of stretching within certain limits did not seem to be of high importance with respect to the degree

of crystallization. All measurements were carried out at a temperature of about 17° C.

At first only scattering results could be obtained, demonstrating clearly the imperfections of the method, which could have been predicted in view of earlier

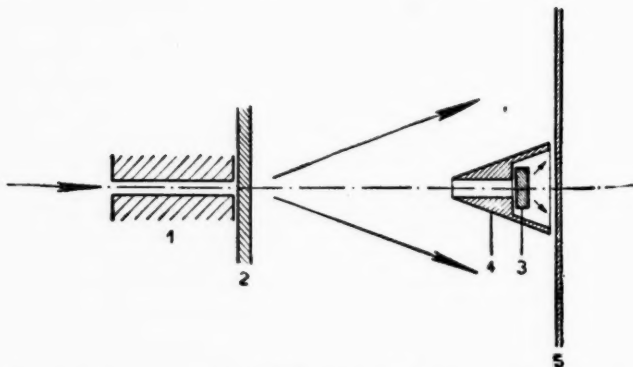


FIG. 1.—Schematic arrangement, suitable for eliminating the influence of undesired fluctuations of primary beam intensity. Another feature of this arrangement is that it permits correcting for air scattering in a very simple and accurate way.

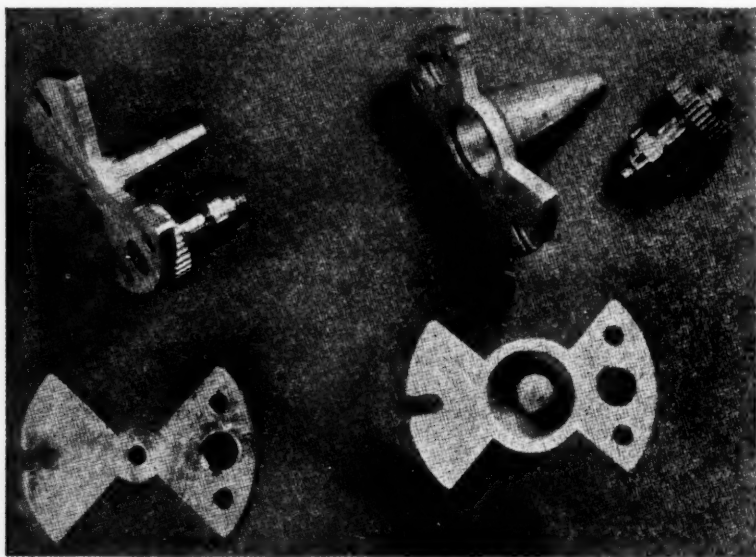


FIG. 2.—Photograph of miniature cameras to obtain a reference intensity in the centre of any x-ray photograph where it is necessary to eliminate intensity variations in the primary beam or to correct for air scattering. If no quantitative measurements are involved, air scattering may be reduced by the small metal cones to the left.

work by Nahmias⁶. It is not only a matter of operating the x-ray tube at a constant radiation output, but the position of the x-ray camera with respect to the tube, and especially the position of the slit with respect to the energy distribution in the primary beam, cannot be reproduced in successive exposures.

Attempts were made to avoid the inaccuracies of the method described above, and these finally resulted in a rather exact one, now to be described in some detail, because it is believed to offer possibilities along other lines of quantitative x-ray analysis.

It has already been emphasized that the x-ray diffraction pattern should contain a reference intensity, virtually permitting corrections for intensity fluctuations of the primary beam. This has been accomplished in a special manner involving a small metal cone, acting in some respects as a miniature camera and mounted as indicated by Figure 1.

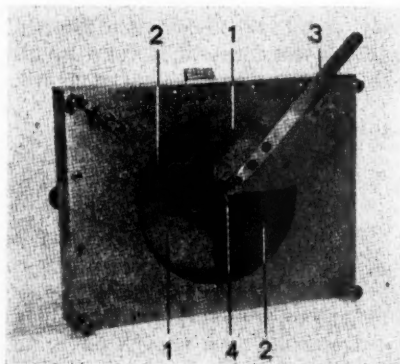


Fig. 3.—Film-holder according to Astbury, equipped with metal cone.

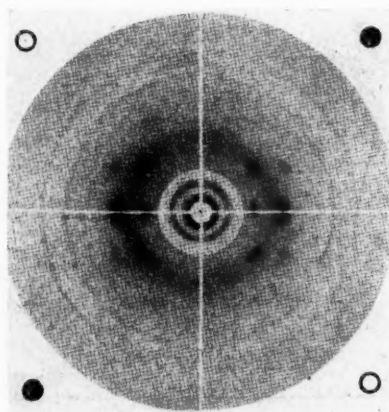


Fig. 4.—x-Ray diagram with reference intensity in the centre of the pattern. Diagram marked O refers to pure-gum vulcanizate, at an elongation of 500 per cent; ● to a sample at an elongation of 550 per cent.

The primary beam, after being limited by the slit 1 and after having passed the rubber specimen under investigation 2, falls on a second sample 3⁸, mounted in a small brass cone 4. The x-ray pattern of sample 3, just as the pattern of the rubber, is obtained on film 5. The metal cone, photographs of which are given in Figure 2, is mounted on a film cassette of a camera type according to Astbury⁴ and Woods⁹ employed throughout this investigation, because it

makes it possible for various types of sample holders to be easily interchanged. The feature of obtaining two x-ray diagrams on one film was also a great advantage, making possible first a speeding up of the work and secondly an easy comparison of two x-ray patterns. A photograph of the mounting of the small metal cone on a film holder is given in Figure 3, while a reproduction of an x-ray diagram, obtained in the way described is given in Figure 4.

The reference intensity I_r in the centre of the diagram may approximately be represented by:

$$I_r = k' I_0 t \exp(-\mu d) \exp(-\mu_r d_r) \quad (5)$$

if I_0 represents the intensity of the primary beam, and $\exp(-\mu d)$ and $\exp(-\mu_r d_r)$, respectively, denote the absorption factors of the rubber specimen and the standard sample. k' is a constant factor depending on the thickness of the reference sample, its scattering power and the choice of other experimental conditions.

It is evident from (2) and (5) that:

$$\frac{I_{a,g}}{I_r} = k'' d_a \quad (6)$$

Thus the ratio, $I_{a,g}/I_r$, does not depend on fluctuations in the intensity of the primary beam and is equally unaffected by absorption, but is directly proportional to the effective thickness of the amorphous rubber.

Intensity measurements were carried out with a direct intensity recording photometer, devised by De Wolff¹⁰. A typical photometer recording is given in Figure 5, where (1) represents the reference intensity, (2) that of the halo, while *a*, *b* and *c* indicate reflections due to zinc oxide crystallites, common components of rubber compounds.

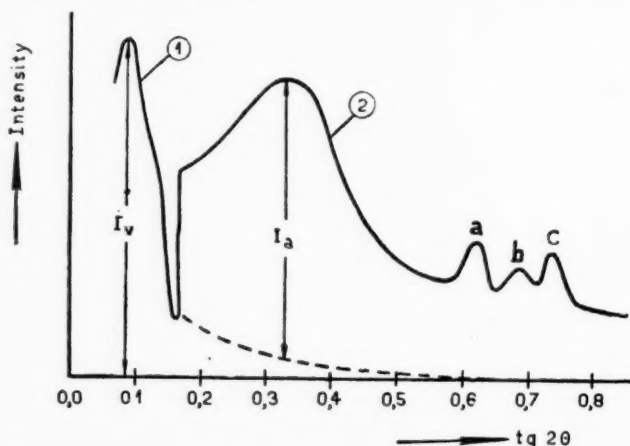


Fig. 5.—A photometer record of an x-ray diagram as reproduced in Figure 4. (1) indicates the reference intensity, (2) the diffuse halo. The dotted line represents the intensity of air-scattering.

Another feature of the method described is that it makes possible corrections for the scattering of x-rays by the surrounding air. This scattering is indicated in Figure 5 by a dotted line and is, of course, proportional to I_r . It may, therefore, easily be determined in any x-ray photograph provided with a reference intensity.

According to Equation (6), $I_{a,g}/I_v$ values are expected to be proportional to the results of direct thickness measurements as long as crystallization has not yet started. Examination of stretched strips of vulcanized rubber actually shows that $I_{a,g}/I_v$ ratios, transformed by multiplication with a constant factor corresponding to $(k'')^{-1}$ from (6), lead to d_a values, identical with d_w values, until an elongation of about 300 per cent is reached. Then crystallization starts and the effective thickness of amorphous rubber d_a decreases more rapidly than d_w does, owing to increasing elongation.

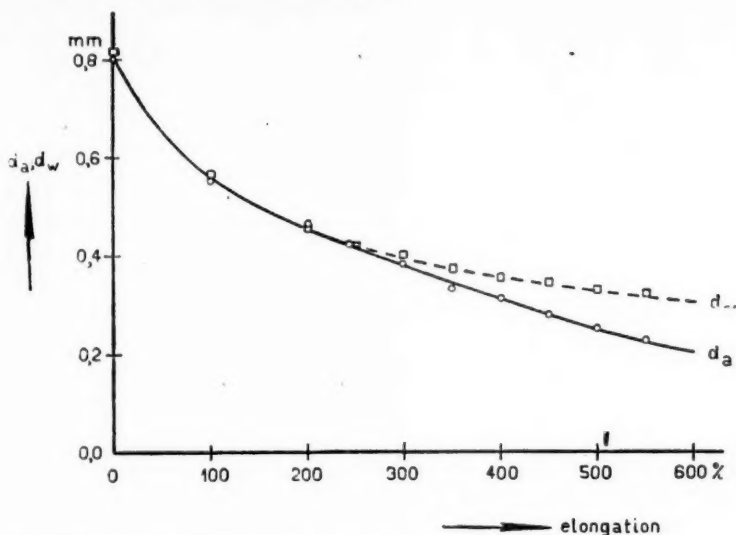


Fig. 6.—Relation between thickness measurements and elongation (vulcanized pure-gum compound). — d_w , as it may easily be calculated from:

$$d_w = \frac{d_0}{\sqrt{\left(1 + \frac{x}{100}\right)}}$$

□ □ actual thickness measurements,

○ ○ x-ray measurements of effective thickness of amorphous rubber.

This is represented by Figure 6 where thickness measurements and x-ray determinations of the amorphous fraction are plotted against elongation.

According to Equation (3) the amount of amorphous rubber A , and consequently the amount of crystalline rubber K , can readily be derived from d_a/d_w ratios. Figure 7 represents the results obtained for a pure-gum vulcanizate¹¹.

It will be noticed that in the foregoing alinea attention was paid only to measurements of the halo intensity, the diffraction spots due to the crystalline rubber being neglected. Simultaneously with the improvement of the halo method, determination of the amount of crystalline rubber by measuring spot intensities was aimed at. It was kept in mind that the ratio, $I_r/I_{a,g}$, is independent of fluctuation in primary-beam intensity and of absorption in the rubber specimen, as was pointed out by Field¹. The ratio of two reflection intensities, corresponding to two components, is always independent of absorption effects if the reflections in question are diffracted at approximately the same glancing angles and if, besides, the mixture is highly dispersed, in case the components have different extinction coefficients for x-rays. With respect to

rubber, only the former condition is important, and it is fulfilled if the spot measurements are carried out at the 201 diffraction spot, corresponding to a spacing of 4.9 Å, as the halo maximum corresponds to a spacing of 4.85 Å. Another advantage of using 201 lies in the fact that this spot is superimposed on a background just where it shows only a small gradient. Therefore the intensity of 201 can be measured more exactly than that of other diffraction spots.

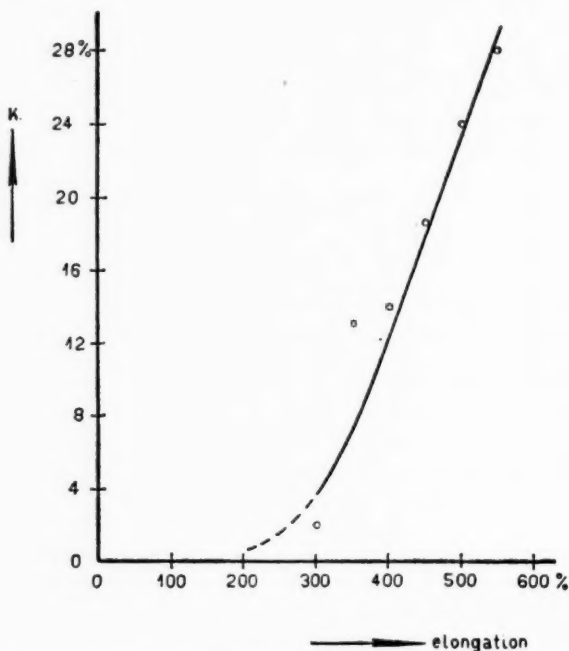


Fig. 7.—The amount of crystalline rubber K plotted against elongation (pure-gum compound).

The maximum intensity I_r measured in the spot is associated with the degree of crystallization K according to:

$$\frac{I_r}{I_{a,g}} = c \frac{K}{100 - K} \quad (7)$$

From any x-ray pattern, even without a reference intensity, K could be easily derived if the value of c were known. Now it would be very difficult, if not impossible, to evaluate c theoretically. The value of c can be determined only by first measuring K in the way described before, and then combining these K values with $I_r/I_{a,g}$ ratios. If this is carried out at different elongations, the same value of c is expected. This has really been found, as illustrated by Table I, giving the calculated c values for a pure-gum vulcanizate.

It may be asked what will be the use of such considerations because the amount of crystalline rubber, the crux of the whole question, has to be known. Indeed, the first aim of using Equation (7) is only to check various starting points. If, however, (7) really represents the relation between the degree of

TABLE I
c VALUES FOR PURE-GUM VULCANIZATE AT DIFFERENT ELONGATIONS

Elongation (%)	$I_r/I_{a,0}$	K(%)	c
0	0.03	—	—
100	0.005	—	—
200	0.03	—	—
250	0.11	—	—
300	0.23	3.5	6.3
350	0.50	7.6	6.1
400	0.85	12.5	6.0
450	1.29	18.0	5.9
500	1.80	24.0	5.7
550	2.42	28.8	6.0

crystallization and the intensity values, there is always a possibility of determining with the aid of a once established c value the degree of crystallinity in other samples in a more accurate and simple way than was possible with the first method.

Indeed the values of c , given in Table I, seem to indicate that Equation (7) holds fairly well, and it may therefore be expected that the degree of crystallization, once determined with the aid of the reference intensity method, can afterwards be derived for other compounds from simple I_r and $I_{a,0}$ measurements.

A complication, limiting the validity of Equation (7), and a modification of that equation, again permitting the use of it, is presented later¹².

Measurements on the amount of crystalline rubber in frozen samples.—It may be emphasized that Equation (6):

$$\frac{I_a}{I_r} = k'' d_a \quad (6)$$

is equally suited for determining the degree of crystallization in samples of frozen raw rubber, a subject not dealt with by Field. A difficulty arises, however, from the fact, that the Debye-Scherrer lines are superimposed on the whole of the diffuse halo, the intensity of which can, therefore, not be measured with sufficient accuracy. This is illustrated by Figure 8, giving photometer records of x-ray patterns of frozen and amorphous raw rubber, represented in Figure 9.

Now Equation (6) holds equally if I_a denotes, not the intensity maximum, but the intensity diffracted at another angle θ_0 . The equation may then be written:

$$\frac{I_a(\theta_0)}{I_r} = k_0 d_a \quad (8)$$

and θ_0 may be chosen in such a manner as to correspond to a halo intensity not complicated by the diffractions of the crystalline rubber, e.g., somewhere between A and B as indicated in Figure 8.

Indeed, it has been possible to determine the degree of crystallization in this way with sufficient accuracy, and the results, together with those obtained on stretched rubber, are described in a later paper¹³.

SUMMARY

There are indications that the degree of crystallization in high polymeric substances is of importance in studying mechanical properties. With regard

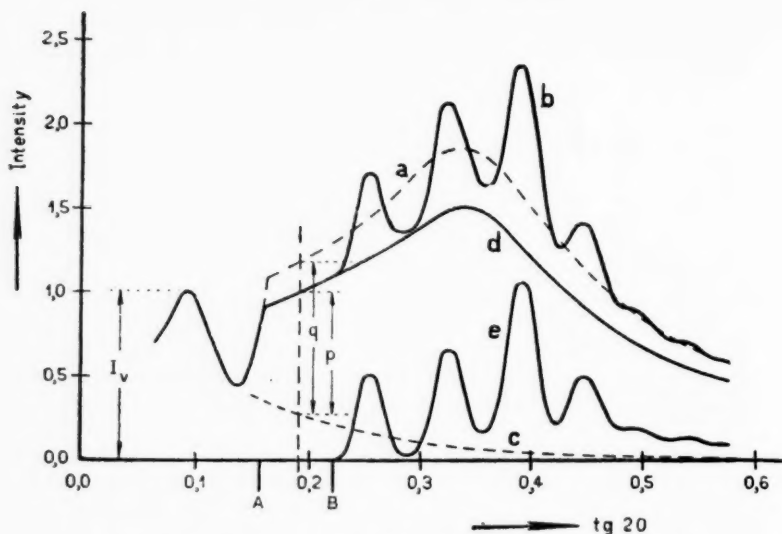


FIG. 8.—Photometer records of x-ray patterns obtained with a first latex crepe.

- a) amorphous crepe } converted to equal I_v ,
 b) frozen crepe
 c) air scattering,
 d) diffraction by amorphous fraction,
 e) diffraction by crystalline fraction.

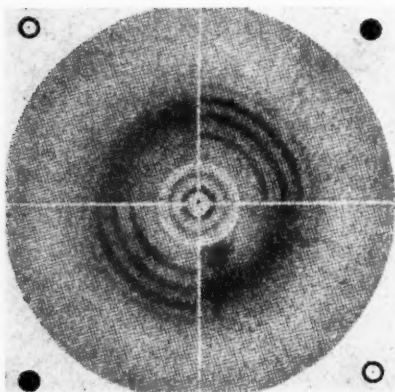


FIG. 9.—x-Ray patterns of first latex crepe. The diagrams marked ● refer to frozen crepe, ○ to the same sample in amorphous state.

to the crystallization of rubber, few measurements have been made, mainly by Field. The results, however, are in contradiction to estimates of an earlier date, and therefore the necessity was felt to have them checked. An x-ray method, in some respects differing from that of Field, was developed, the results of which diverged considerably from the figures reported by Field. The present article deals with a description of the method.

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- ⁴ The notation is the same as that used in the original Dutch thesis ("Quantitative Röntgenografische Onderzoekingen aan Rubber", Delft, 1946).
- ⁵ Nahmias, *Z. Krist.* **83**, 329 (1932); Clark and Reynolds, *Ind. Eng. Chem. Anal. Ed.* **1**, 36 (1936).
- ⁶ Nahmias, *Z. Krist.* **83**, 329 (1932).
- ⁷ Holt and McPherson, *J. Research Natl. Bur. Standards* **17**, 657 (1936); *RUBBER CHEM. TECH.* **10**, 412 (1937).
- ⁸ A powder comprised of aluminum hydroxide and calcium sulfate was used as a reference sample.
- ⁹ Astbury and Woods, *Trans. Roy. Soc. (London)* **A232**, 333 (1934).
- ¹⁰ De Wolff, unpublished work.
- ¹¹ This vulcanizate was prepared from a mixture of rubber 100, sulfur 1.75, diphenylguanidine 0.5, mercapto-benzothiazole 0.8, aldol- α -naphthylamine 1, stearic acid 1, and zinc oxide 5 parts, cured 30 minutes at 142° C.
- ¹² See following paper in this issue of *RUBBER CHEMISTRY AND TECHNOLOGY*.
- ¹³ This paper will be Part III of this series, and will be published in *Applied Scientific Research*.

II. THE ORIENTATION OF RUBBER CRYSTALLITES IN STRETCHED SAMPLES

Introduction.—In Figures 1 and 2, the x-ray patterns of stretched vulcanized rubber compounds are reproduced. Figure 1 refers to a rubber-benzoyl peroxide compound¹, Figure 2 to a rubber-*p*-cresoldialcohol compound². A mere look at the x-ray patterns of these compounds shows the differences in the degree of crystallite orientation. Now, in the preceding work, the degree of crystallization was linked up with the maximum spot intensity, and broadening

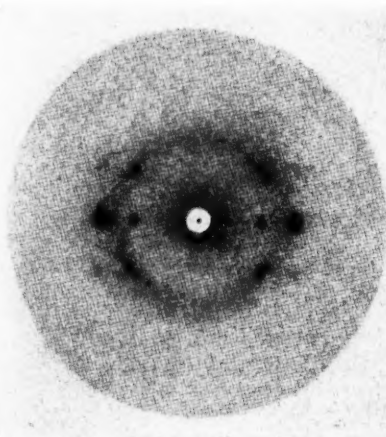


FIG. 1.—x-Ray diagram of a rubber-benzoyl compound.

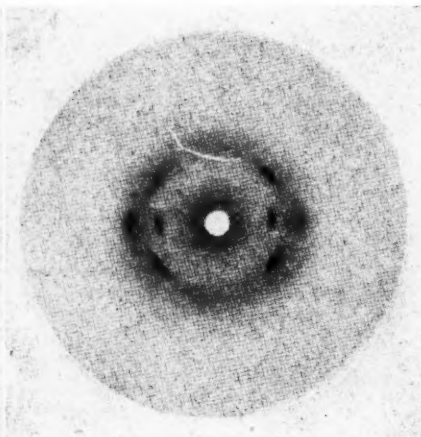


FIG. 2.—x-Ray diagram of a rubber-*p*-cresoldialcohol compound.

of the spots was not taken into consideration. The factor c from Equation (7) is, therefore, somehow connected with the orientation of the crystallites, and an attempt will be made to find out whether this relation can be derived.

Orientation of the crystallites.—The variation of intensity along a Debye-Scherrer line in patterns of substances not randomly crystallized, such as

cellulose fibers, is associated with distribution curve $N(\varphi)$ by Kratky³:

$$I_r(\epsilon) = \int_{\epsilon}^{\pi/2} N(\varphi) \frac{\sin \varphi}{\sqrt{(\sin^2 \varphi - \sin^2 \epsilon)}} d\varphi \quad (1)$$

In this equation φ denotes the deviation of the crystal axis from the direction of stretch, $N(\varphi) \sin \varphi$ the number of crystallites having an orientation between φ and $\varphi + d\varphi$ and ϵ the angle between the plane of incident radiation and diffracted beam, the intensity of which is being considered, and the plane perpendicular to the direction of stretching. If only comparatively small deviations from this direction are considered (low φ -values) and if $N(\varphi)$ is supposed to be represented by:

$$N(\varphi) = a \exp(-b^2 \varphi^2) \quad (2)$$

it can be shown that Equation (1) may be written as

$$I_r(\epsilon) = I_{rmax} \exp(-b^2 \epsilon^2) \quad (3)$$

I_{rmax} denoting a constant factor⁴. In that case I_r too would be represented by a Gauss curve, differing only in height, not in breadth from (2). As the results of tangential intensity, measurements can actually be represented by a curve corresponding to (3), as illustrated by Figure 3, $N(\varphi)$ may be assumed to be

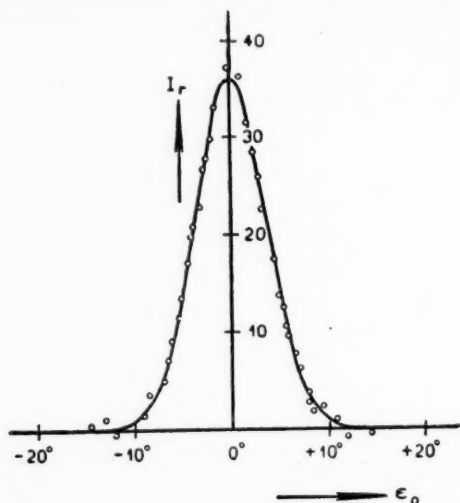


Fig. 3.—Tangential intensity measurements (diffraction spot 201) pure-gum compound, at an elongation of 550 per cent.
— curve according to (3),
..... photometer readings.

represented by (2), in which case the crystallite orientation, indicated by the value of b , may be readily obtained from intensity measurements. For the sake of simplicity the degree of orientation is denoted by a half-intensity angle φ_1 which is easily derived from photometer readings, defined by $N(\frac{1}{2}\varphi_1) = \frac{1}{2}N(0)$ and related to the value of b by $b^2\varphi_1^2 = 4 \ln 2$.

The values indicating the orientation of the crystallites in a pure-gum compound were found to be practically independent of the elongation, as is evident from Table I.

TABLE I

 φ_1 -VALUES OF A PURE-GUM COMPOUND AT DIFFERENT ELONGATIONS

Elongation (%)	φ_1 (°)			
	350	500	550	600
350	8.5	8.8		
500	8.3	8.8	8.2	8.7
550	8.5	8.5		
600	8.6	8.5		

Vulcanizates showing higher φ_1 -values (15–18°) have their crystallites somewhat better oriented as elongation increases. The corresponding decrease in φ_1 amounts only to 1–2°. At first sight the approximate constancy of the crystallite orientation seems strange and in contrast to the wide range of the degree of orientation of the crystalline regions in differently stretched samples of fibre materials, such as viscose rayon. In rubber and a few allied substances, the crystallites come into existence when the molecules are already to some extent oriented, though this does not yet offer a satisfactory explanation for the observed constancy. To explain this, it may be assumed that the crystallites once formed are imbedded in a molecular network, thus building a rigid structure in which increasing elongation cannot bring about higher orientation.

It is also possible, in view of the presence of long entangled molecules, that stretching may simultaneously produce orienting and disorienting effects which could account for the constancy of φ_1 .

Measurements of φ_1 were carried out on various vulcanized rubber compounds. A remarkable correlation turned out to exist between the crystallite orientation and the modulus. In Figure 4 the φ_1 values, measured with an ac-

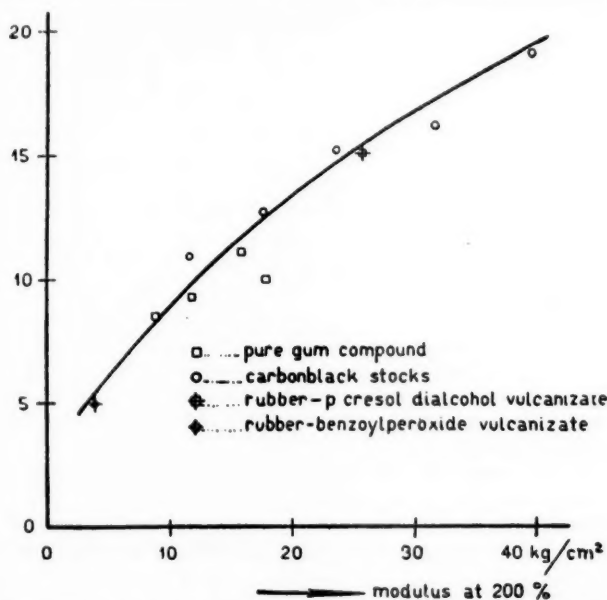


FIG. 4.—Relation between the degree of orientation of the crystallites in stretched samples, characterized by the value of φ_1 and the modulus at 200 per cent elongation.

curacy of about 0.3° , are plotted against the moduli at 200 per cent elongation. This relation will be discussed in a later paper⁵. For the present purpose it is sufficient to notice that different values of the degree of orientation have been observed, ranging from 5 to 18° , and that therefore any method of deriving the degree of crystallization from spot intensities is bound to lead to erroneous results if crystallite orientation is not taken into account.

Eliminating errors owing to crystallite orientation.—As already pointed out, the degree of orientation of rubber crystallites has to be taken into account when determining the crystallinity of rubber, and to avoid errors in this respect, it is necessary to use integrated spot intensities, instead of their maximum values. Equation (7) of the previous work must be written as:

$$\frac{\iint I_r(\epsilon, 2\theta) d\epsilon d2\theta}{\iint I_{a,g}(\epsilon, 2\theta) d\epsilon d2\theta} = c' \frac{K}{100 - K} \quad (4)$$

In this equation, θ denotes the glancing angle and ϵ , just as before, the polar angle from the center of the x-ray pattern in the plane of the film (see Figure 5).

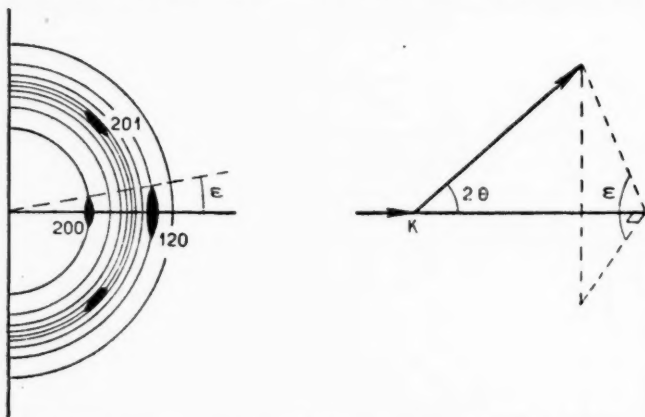


FIG. 5.—Schematic representation of (1) x-ray pattern, (2) x-ray diffraction.

Now one may start from the following assumptions:

- (1) $I_r(\epsilon, 2\theta) = I_r\Phi_1(\epsilon)\Phi_2(2\theta)$, which means that the radial half intensity breadth of the diffraction is independent of ϵ .
- (2) $I_{a,g}(\epsilon, 2\theta) = I_{a,g}\Phi_2(2\theta)\Phi_4(\epsilon)$.

Rubber compounds of diverging composition, including pure-gum vulcanizates and carbon-black mixtures, were examined to determine whether important differences in $\Phi_2(2\theta)$ are present. If the functions Φ_2 are characterized by a half-intensity breadth, values of $(2\theta)_\frac{1}{2}$ are found ranging from 0.025 to 0.027 radians.

In view of the results obtained by Iguchi and Schoszberger⁶, indicating only a slight variation of $I_{a,g}$ with ϵ , it seems justified to suppose $\Phi_4(\epsilon)$ identical for many rubber compounds. Our own measurements indicate that a large group of rubber compounds have practically identical $\Phi_2(2\theta)$ functions. This is understandable because the compounds examined consisted principally of rubber. When important amounts of loading agents (carbon black) were present, corrections for the corresponding extra scattering were made.

In view of the above considerations, Equation (4) can be written in the approximate form:

$$\frac{I_r}{I_{a,0}} \int \Phi_1(\epsilon) d\epsilon = c'' \frac{K}{100 - K} \quad (5)$$

Thus the constant c in Equation (7) of the earlier work⁷ turns out not to be constant at all, but to depend on the degree of orientation. It has been pointed out that $\Phi_1(\epsilon)$ can be represented by:

$$\Phi_1(\epsilon) = \exp(-b^2\epsilon^2) \quad (3)$$

Now combination with Equation (7) of the earlier work⁷, (3) and (5) gives:

$$c = \frac{c''}{\int \Phi_1(\epsilon) d\epsilon} = bc''$$

and as $b^2\varphi_1^2 = 4 \ln 2$, there results:

$$c = \frac{c_0}{\varphi_1} \quad (6)$$

Owing to differences in the degree of orientation, the value of c is not the same for every compound. Having once evaluated c in the case of a certain compound, φ_1 measurements make possible the use of Equation (7) of the earlier work⁷, by permitting an easy calculation of c from Equation (6).

It would be more exact, of course, if in Equation (5) $\int \Phi_1(\epsilon) d\epsilon$ were replaced by $\iint \Phi(\epsilon, 2\theta) d\epsilon d2\theta$, but an integration of the spot intensity is very difficult. However, for the present purpose of obtaining a correction for Equation (7) of the earlier work⁷, the approximation is sufficient. More refined future experiments may necessitate the use of more exact formulas.

Check on the foregoing discussions.—The vulcanized pure-gum compound, with a c value of 6.0, has a crystallite orientation characterized by a φ_1 value of 9.8°. From these figures the value of c_0 is $6.0 \times 9.8 = 59$. Now in view of the various assumptions and approximations underlying the foregoing considerations, it is desirable to undertake measurements of other rubber compounds, with different φ_1 values, to check the validity of Equation (6).

For this purpose a carbon black compound was chosen⁸, because this displays the highest measured φ_1 value, 18°. A difficulty arises from the presence of carbon black in such proportions that it superimposes a strong x-ray pattern on the rubber pattern. Corrections are, of course, necessary to derive the actual rubber halo intensity from the photometer recordings. Therefore a mixture was composed, containing all the ingredients of the carbon black compound except the rubber. An x-ray diagram was taken of this mixture, and the results of the intensity measurements are represented in Figure 6 and indicated by curve 2.

The curve denoted by 1 represents the diffraction by the vulcanized unstretched carbon black compound. Of course curve 2 does not represent the actual diffraction by the nonrubber ingredients of the compound, because the diffracting amount will not be just the same as present in the vulcanized stock. The intensities of the zinc oxide lines now make possible a transformation from 2 to 3 in such a manner that these intensities become as strong as in the vulcanized compound. Curve 3 then represents the actual diffraction caused by the nonrubber components, so that the measured halo intensity must be re-

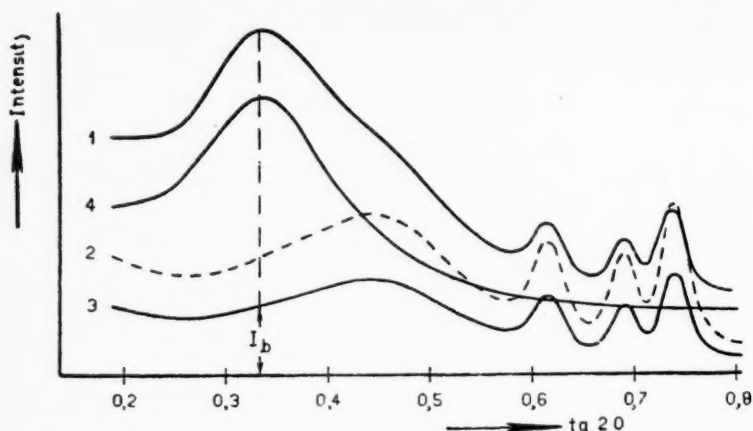


FIG. 6.—x-Ray diffraction by a vulcanized carbon black compound, unstretched (1). Diffraction by vulcanizing ingredients, except rubber (2 and 3). Diffraction by the rubber (4).

duced by an amount I_b . It may be noticed that Field, also dealing with carbon black compounds, does not mention the necessity of any correction.

The results, obtained in the way described in the earlier work⁷, are given in Table II. With the values of $\varphi_1 = 18^\circ$, the mean value $c = 3.4$ from Table II

TABLE II
DEGREE OF CRYSTALLIZATION K , AND THE VALUE OF c AT DIFFERENT
ELONGATIONS OF A CARBON BLACK COMPOUND

Elongation (%)	K (%)	$\frac{I_r}{I_{a,0}}$	c
250	7	0.23	3.0
350	12	0.48	3.5
400	14	0.57	3.5
450	17	0.67	3.4

gives $c_0 = 3.4 \times 18 = 61 \pm 4$. Compared with the c_0 value for the pure-gum compound ($=59$) the deviation is remarkably small, which is in support of the method, according to which the degree of orientation is involved the interpretation of the intensity measurements.

Next it was desirable to check the method by measurements on another rubber compound of a strongly diverging composition. A rubber *p*-cresoldi-alcohol compound was chosen⁹. The orientation of the crystallites in this compound can be given by a φ_1 value of 15° , and the intensity measurements lead to a c value of 3.5, combination of which leads to $c_0 = 3.5 \times 15 = 52.5$. In this case the deviation from the values 59 and 61 for a pure-gum and a carbon black compound is not to be neglected. It must, however, be kept in mind that the compound in question is a rather unusual one. Moreover, only a correction on the use of the unmodified Equation (7) of the earlier work was aimed at, and, generally speaking, the way in which the method accounts for the variations in the degree of orientation is satisfactory.

ACKNOWLEDGMENT

In a third article the author intends to present the results, obtained with the method described, and to discuss them in detail. He wishes to acknowl-

edge the helpful discussions with A. van Rossem, who also kindly supplied valuable samples of raw and vulcanized rubber, and with H. B. Dorgelo, both of the Delft University. Their continued interest is very much appreciated.

Thanks finally are due to the Delft University Fund for its support of this research and to the directors of the Rubber Foundation for their permission to publish the results.

SUMMARY

In the foregoing article a method for determining the proportion of crystalline rubber in stretched samples has been described. A complication due to varying crystallite orientation in different samples appeared to interfere with the application. A simple relation is given between the degree of orientation and an empirical constant which makes possible a rapid determination of the degree of crystallization, regardless of the orientation in the sample under investigation.

REFERENCES

- ¹ This compound had the following composition: crepe rubber 100 and benzoyl peroxide 10 parts, vulcanized 20 minutes at 147° C.
- ² This compound had the following composition: crepe rubber 100, *p*-cresoldialcohol 40 parts, vulcanized 120 minutes at 155° C.
- ³ Kratky, *Kolloid-Z.* **64**, 213 (1933).
- ⁴ This equation was derived for reflecting planes parallel to the direction of stretching. Since other than equatorial reflections are considered, the approximation presented by Equation (3) is the better.
- ⁵ This paper will be Part III of this series and will be published in *Applied Scientific Research*.
- ⁶ Iguchi and Schosberger, *Kautschuk* **12**, 193 (1936).
- ⁷ See Part I (preceding paper of this issue of RUBBER CHEMISTRY AND TECHNOLOGY).
- ⁸ This compound had the composition: rubber 100, sulfur 2, diphenylguanidine 0.5, mercaptobenzothiazole 0.8, aldol- α -naphthylamine 1, stearic acid 2, lubricating oil 2, asphalt 8, carbon black 44, cured 30 minutes at 142° C.
- ⁹ This compound had the following composition: rubber 100, *p*-cresoldialcohol 40, and was cured 20 minutes at 155° C.

COMPARATIVE STUDIES ON PHOTOELASTICITY OF ELASTOMERS AND PLASTOMERS *

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Transparent films of elastomers and plastomers were found to differ sufficiently in their photoelastic behavior to make stress double refraction a useful criterion of the prospective mechanical properties of a given material. The stress double refraction in such films is mostly an effect of deformation, of orientation, or of both deformation and orientation of polymer chains. In such polymers, however, which crystallize under stress, a large part of the optical effect may be due to oriented crystallization. In addition to its practical value as a testing method for polymers, the photoelastic method offers, therefore, particularly in combination with simultaneous investigations of mechanical properties, the prospect of correlating mechanical properties of a polymer film with its internal structure, and of correlating changes in both qualities on exposure of the film to different degrees of stress. Although results obtained on such films, by means of x-ray diffraction or x-ray scattering and electron-diffraction, are, in general, easier to interpret, the photoelastic method has the considerable advantage of making possible a quantitative follow-up of rapid changes in film structure, *e.g.*, of relaxations.

Figure 1 gives a survey of the apparatus used. Its comprehensive description, and an extensive presentation and discussion of the results obtained with it, will follow in a paper to be published later¹. The purpose of the present preliminary account is to illustrate selected aspects of the potentialities of the method in comparative investigations, with particular reference to polythene (polyethylene)².

A comparatively simple type of photoelastic investigation, by means of which characteristic differences between elastomers and plastomers and, in addition, differences between noncrystallizing and crystallizing elastomers can be detected, is the study of double refraction as a function of elongation of a film. The film, generally 180–250 μ thick, is clamped firmly in slipproof jaws of an electrically operated stretching device, and is extended, normally to the direction of the light beam, to any elongation desired within the available range. The elongation, ΔL_s , is expressed in percentage of the original length of the sample, *i.e.*, $\Delta L_s = \frac{(L_s - L_o)}{L_o} \times 100$, where L_o is the original length of

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the sample and L_s is its length under stress. Both lengths are known with an accuracy of better than 1 per cent. Unless stated otherwise, the film remains under stress during the optical investigation, which is carried out with a polarizing microscope provided with a synchronous polarizer-analyzer movement and with an ellipticity compensator (sensitivity limit of compensator: a path difference, Δ , of 30 Å.). To have numbers of a convenient order of magnitude, the path difference is expressed in $\mu/\text{mm.}$ of polymer thickness. The value of $(n_e - n_o)$ is easily obtained from Δ by multiplying it by 10^{-2} . The values obtained are valid for 5461 Å. and for room temperature ($23^\circ\text{--}25^\circ\text{C}$).

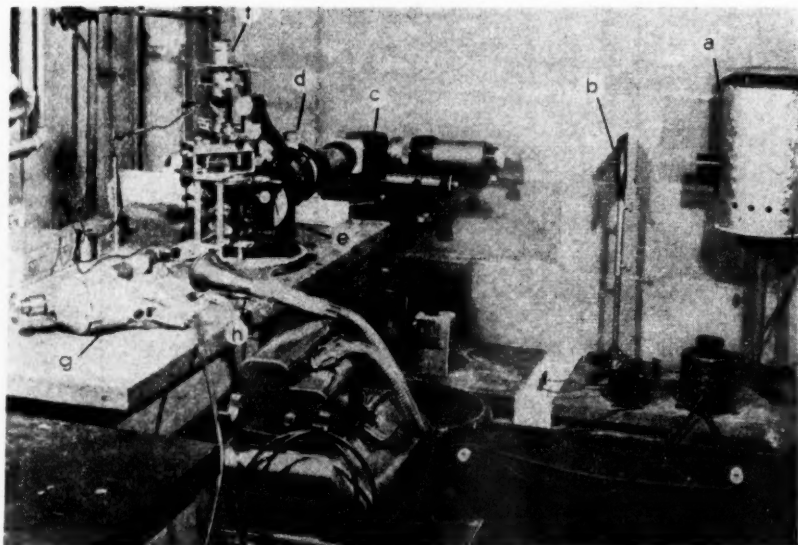


Fig. 1.—Apparatus for the study of stress double refraction in films.

a, Light source (tungsten ribbon filament lamp); b, collimating lens; c, monochromator; d, heat filter; e, condensing lens; f, polarizing microscope with mounted stretching apparatus; g, drill for rapid stretching of film. (Disengages automatically at any desired elongation.) Applied at (f); h, dictaphone for the recording of rapid successive measurements.

Figure 2 gives the type of results obtained. They apply to the optical effect observed in the samples under stress, Δ_s , after changes with time (see below) have gone to practical completion (symbolized by the additional subscript: f). It may be mentioned that each experimental point, both here and in subsequent figures, excepting Figure 4, was obtained with a different sample cut from the same film in bulk. This accounts for the scattering of the experimental points which, on the whole, is moderate. Noncrystallizing elastomers, such as GR-S, show a nearly linear increase of birefringence with elongation up to the elongation where rupture of the film occurs (Curve I). Crystallizing polymers, such as cured natural rubber, show the same behavior at sufficiently small elongations. At higher elongations, however, crystallization leads to a steep increase in birefringence with elongation. The complete curve is, therefore, characterized by a fairly strong increase in slope at intermediate elongations (Curve II). Plastomers, such as polythene, finally, exhibit curve type III, i.e., they show a very steep increase of double refraction at low elongations, followed, at moderate elongations, by an approach to saturation. At low

elongations (ΔL , of less than 150), the double refraction is, at least in polythene, of an order of magnitude larger than in either type of typical elastomers. This difference is far too large to be accounted for by differences in the optical anisotropy of chain elements in polythene compared to rubbers. Nor does it seem to be possible to explain this difference by a strong difference in the degree of elastic deformation of cross-linked chains. It seems to be necessary, therefore, to assume that, at comparable elongations, a far better orientation of polymer chains takes place in plastomers than in elastomers³.

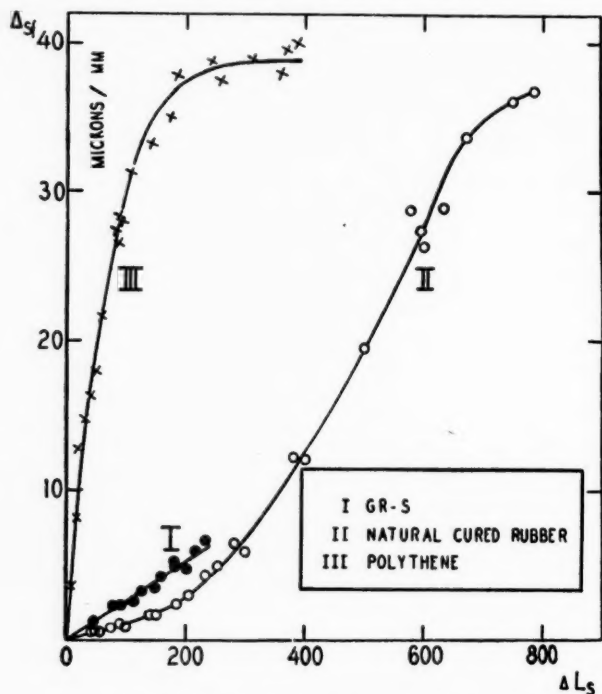


FIG. 2.—Variation of final double refraction with elongation.

Another method of differentiation between the various type of polymer films is illustrated by Figure 3. It shows the change of double refraction with time, t , subsequent to rapid extension of a film, the latter requiring less than one second for a $\Delta L_s \leq 400$ and less than 2 seconds for a $\Delta L_s \leq 800$. Curve I refers to elastomers which do not crystallize. Here, the double refraction decreases with time at constant elongation, and for all ΔL_s values, particularly during the first 20 seconds following stretching. Again, crystallizing elastomers show the same behavior provided the elongations, ΔL_s , are kept below those which cause crystallization (Curve IIa). At higher elongations, crystallization leads to an increase in double refraction with time (Curve IIb). (Special experiments seem to indicate that a decrease of double refraction with time occurs also for the higher elongations, but it is overshadowed by the far larger opposite effect.) Thus, very complex curves result if the double refraction is measured in a gradually extended and subsequently gradually retracting sample. Two pointed hysteresis loops are then obtained which touch each other at

a moderate elongation (Figure 4). The existence of these two consecutive loops, of which only the more pronounced one, due to crystallization, seems to have been observed previously⁴, agrees with the calorimetric results obtained on crystallizing polymers by Guth and associates⁵. In contradistinction to typical elastomers, polythene does not show any detectable change of double refraction with time, at least not after completion of rapid extension (Figure 3, Curve III).

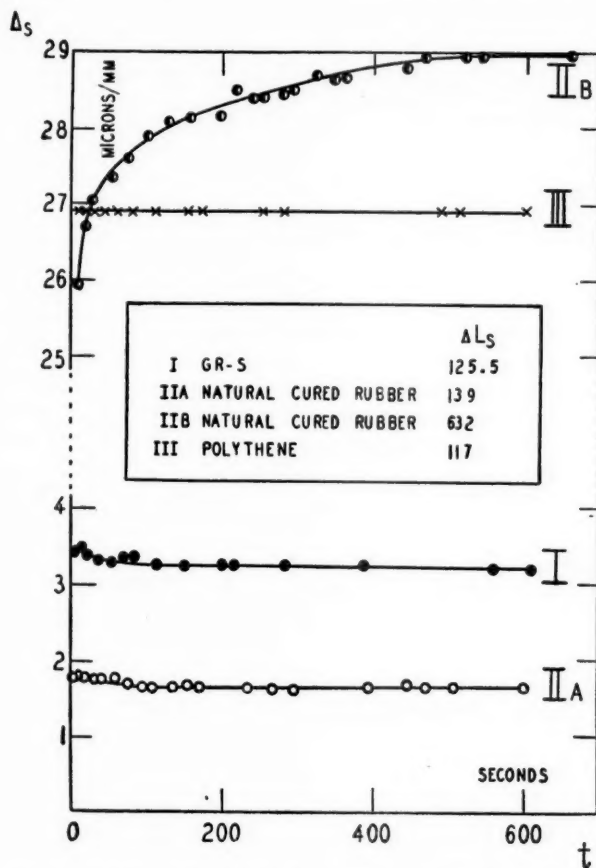


Fig. 3.—Variation of double refraction with time at constant elongation.

Of particular interest is the combined investigation of mechanical retraction and optical relaxation of polymer films after complete release of stress, which leads to a length $L_r > L_0$ and to a permanent residual path difference $\Delta_r > \Delta_0$ ($\Delta_0 = 0$ for the samples used). The discussion of this point will be limited to the special case of polythene. Figure 5 shows the residual increment in length, $\Delta L_r = [(L_r - L_0)/L_0] 100$, as a function of ΔL_s . Figure 6 gives Δ_r as a function of ΔL_s , and Figure 7 illustrates the variation of Δ_r with Δ_s . The three figures refer to the same series of samples. Their comparative discussion leads to the following conclusions.

(1) Polythene is predominantly elastic at low elongations.

(2) Extensive plastic flow sets in, according to Figure 5, above a certain moderate elongation. It is accompanied by a steep increase in permanent double refraction (Figures 6 and 7), which indicates a strong rise in irreversible orientation of polymer chains⁶. Although the present data do not allow a differentiation between cause and consequence, a hypothesis seems to be inviting to the effect that a critical degree of stress-induced, largely reversible, chain alignment is necessary and sufficient to start, on further increase in stress,

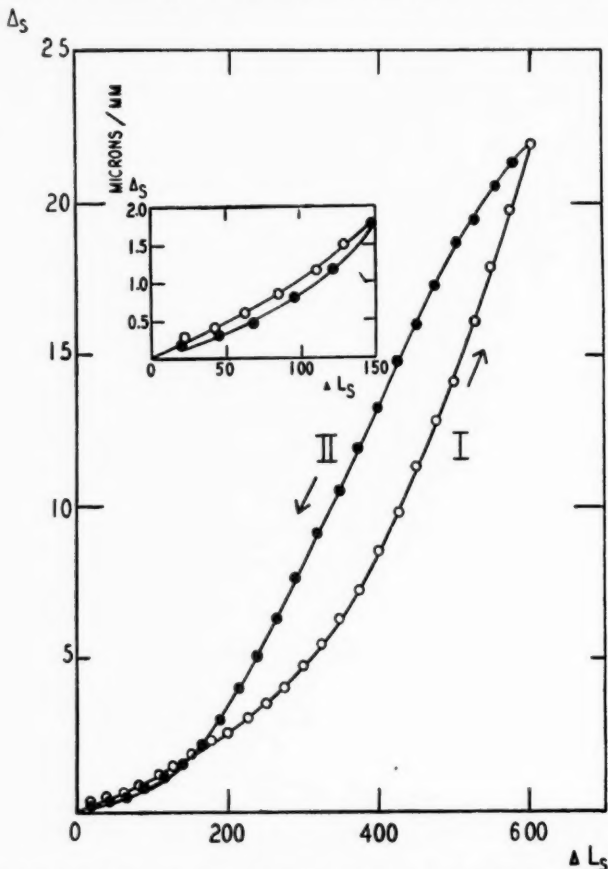


FIG. 4.—Variation of double refraction with elongation, in natural cured rubber, under simultaneous variation of time.

I. Partial successive extensions; II. subsequent, partial successive retractions. (The time interval between the successive changes in elongations, and between the successive optical measurements, was 2.0 minutes throughout.)

an extensive plastic flow and to bring about, simultaneously, an extensive, though incomplete, further and largely irreversible alignment of polymer chains.

(3) Notwithstanding the fact that plastic flow is the predominant feature if polythene is stretched beyond a critical range of elongations, a pronounced elastic retraction occurs also above the latter range. The practically constant

value of nearly 1 of the slope in Figure 5 indicates that the absolute degree of elastic retraction (*i.e.*, the absolute decrement in length ($L_s - L_r$)) is then independent of elongation. The relative degree of retraction (*i.e.*, the decrement in length in percentage of the length before retraction), however, decreases very strongly with increasing elongation. A nearly inverse behavior is found at comparable elongations for typical elastomers, such as cured natural rubber and GR-S. Here, the relative degree of retraction is nearly independent of elongation—considering the status reached one hour after the release of stress—and the absolute degree of retraction increases with elongation. Polythene behaves similarly at elongations below the critical range.

The absolute degree of retraction may be taken as a rough indication of the magnitude of the restoring force. It therefore appears that the restoring force in polythene changes little, if at all, with elongation, in the range where plastic flow predominates, whereas it increases with elongation below the critical range of elongations. In contradistinction, the restoring force in cured natural rubber increases with elongation throughout the range investigated (largest ΔL_s : 785).

Preliminary studies on polythene suggest that there is also a correlation between the magnitude of the restoring force and the rate of optical relaxation which follows a rapid partial retraction. Here the samples are allowed to retract only partially, from a length L_s to a length L_{p1} . After a sufficiently long time, they are allowed to carry out a second partial retraction, from L_{p1} to L_{p2} , and so on. The relative degree of each successive partial retraction is kept equal, that is:

$$[(L_s - L_{p1})/L_s] \times 100 = [(L_{p(n-1)} - L_{pn})/L_{p(n-1)}] \times 100 = \Delta R = \text{constant.}$$

TABLE I

VARIATION OF OPTICAL RELAXATION TIME, τ' , WITH PROGRESSIVE PARTIAL RETRACTION OF POLYTHENE

$$\Delta R: 20.0; \text{Series A. } \Delta L_s: 50.0; \Delta s_f: 15.1 \mu/\text{mm. } \Delta L_p = \left(\frac{L_{pn} - L_o}{L_o} \right) \times 100$$

n (successive steps)	ΔL_p	$\Delta p_n f$ ($\mu/\text{mm.}$)	γ_n ($\mu/\text{mm.}$)	τ' (sec.)
1	40	13.5	1.6	<5
2	32	12.0	1.5	<5
3	25.6	10.95	1.05	<5
4	20.5	9.65	1.3	<5
5	16.4	8.6	1.05	<5
6	13.1	7.0	1.6	<5
7	10.5	5.9	1.1	<5
8	8.4	4.4	1.5	10
9	6.7	3.3	1.1	20
10	5.4	0.5	2.8	540
Series B. $\Delta L_s: 80.0; \Delta s_f: 23.8 \mu/\text{mm.}$				
1	64	21.35	2.45	<5
2	51.2	20.0	1.35	<5
3	40.9	18.1	1.9	<5
4	32.8	16.45	1.65	<5
5	26.2	14.7	1.75	<5
6	20.95	12.7	2.0	<5
7	16.8	11.6	1.1	<5
8	13.4	9.85	1.75	~5
9	10.75	8.45	1.40	10
10	8.6	7.35	1.1	50
11	6.9	6.0	1.35	215

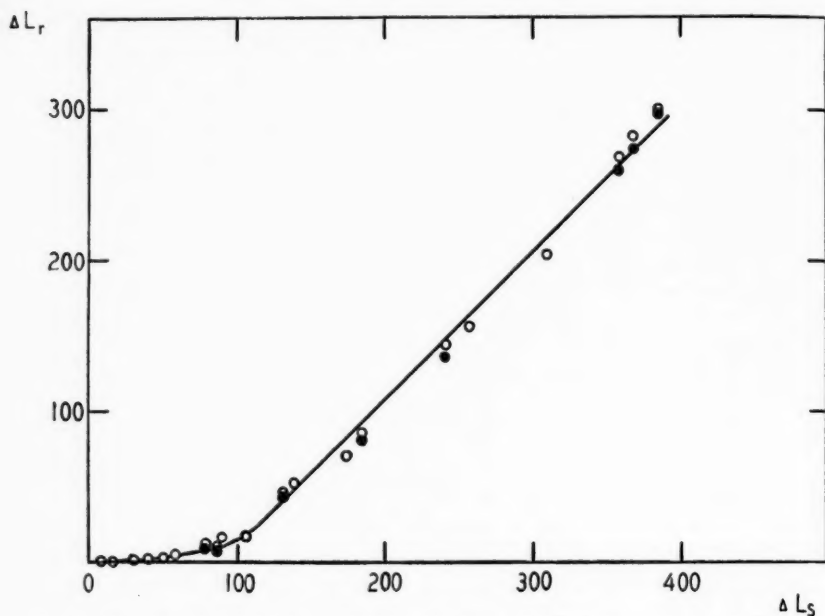


FIG. 5.—Variation of mechanical retraction with the degree of preceding elongation of polythene.
 ○ 24 hrs. after release of stress. ● 12 days later.

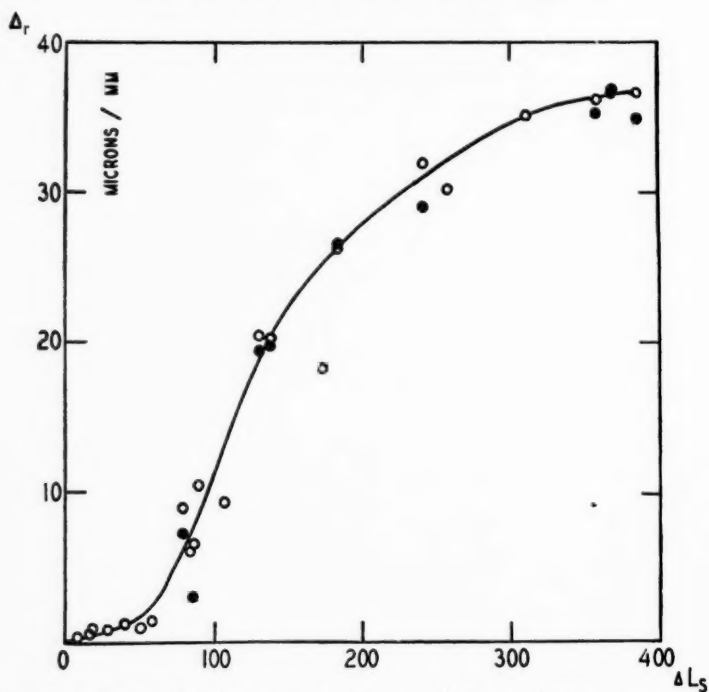


FIG. 6.—Variation of residual (permanent) double refraction in retracted polythene with preceding elongation.
 ○ 24 hrs. after release of stress. ● 12 days later.

Such experiments show that the practically instantaneous partial mechanical retraction is not accompanied by an equally rapid adaptation of birefringence to the reduced elongation. The optical effect continues to decrease with time, particularly during the first minute after partial retraction. One may, for practical purposes, define a relaxation time, τ' , which represents the time necessary to reach $1/2$ (instead of $1/e$ which would characterize τ) of the decrement $\gamma_n = (\Delta p_{(n-1)} - \Delta p_n)$. Thus $\gamma_1 = (\Delta_s - \Delta p_1)$. It is then found with polythene that τ' , whenever it is large enough to be measured, increases strongly with the decrease of L_p , ΔR being constant. Table I shows a few of the results obtained considering ΔL_s values of 50 and 80, respectively. In both cases, $\Delta R = 20$. Since both ΔL_s values considered fall into the range of elongations where polythene behaves predominantly as an elastomer, it appears that τ' , whenever it is measurable, decreases as the restoring force increases. It is noteworthy that τ' was immeasurably small throughout the range of elongations which lead to predominant plastic flow.

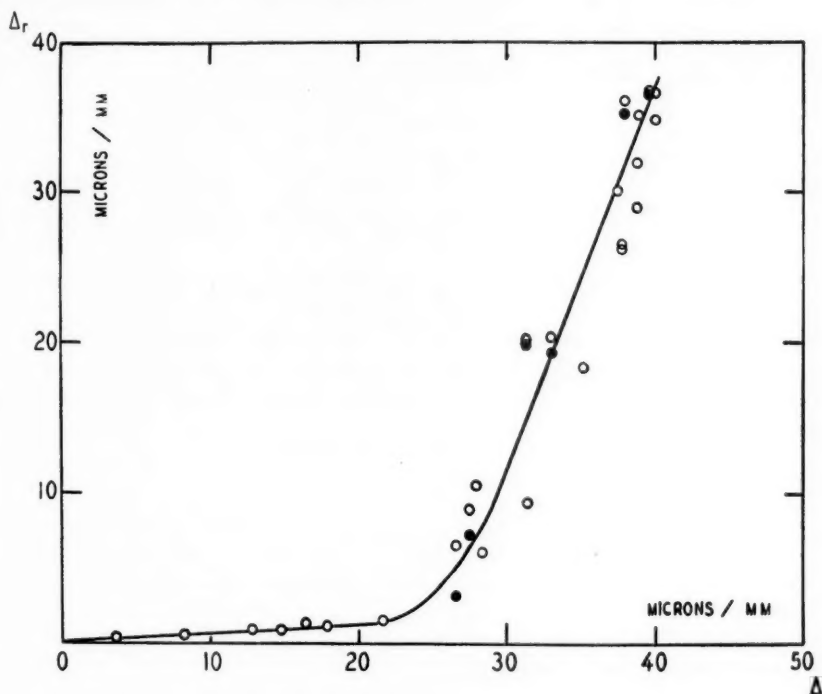


Fig. 7.—Variation of residual double refraction in retracted polythene with the double refraction observed prior to retraction.

○ 24 hrs. after release of stress. ● 12 days later.

The technique of successive partial retraction makes it possible to compare, at equal elongations ΔL_p , the double refraction of samples which had previously been brought to unequal higher elongations, ΔL_s and $\Delta L_s'$, respectively. As an example, Series I and Series II of Table I yield, by interpolation, a final path difference of 13.5 and 17.9 $\mu/\text{mm.}$, respectively, on partial retraction to a ΔL_p of 40, and a final path difference of 9.5, and 13.0 $\mu/\text{mm.}$, respectively, on

further partial retraction to a ΔL_p of 20. Thus, samples of comparable length have a more anisotropic structure, the larger the elongation to which they had been brought previously. In addition, it can be seen from Table I that the relaxation time, τ' , is, at a given ΔL_p , larger, the larger the original elongation, ΔL_o . Finally, Figures 5 and 6 have shown that both the permanent increase in length of a sample, ΔL_r , and its permanent birefringence, Δ_r , are larger, the larger the original elongation. Since the double refraction and, implicitly, the structural anisotropy are larger the larger the elongation (see Figure 2), it follows that (1) the ability of a polythene film to rearrange its structure in the direction of random distribution of individual chains and in the direction of a strain-free configuration of chain elements and side chains, and (2) the rate of this structural rearrangement, are less, in comparable states of retraction, the larger the original stress-induced structural anisotropy.

The usefulness of comparative photoelastic investigations was increased considerably by including recently, in the techniques outlined, simultaneous measurements on the variation of double refraction with a numerically known stress, *i.e.*, curves of the type compiled previously by other authors, *e.g.*, by Thibodeau and McPherson⁷. Results obtained on polythene by means of the latter technique will be described in the near future.

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- ¹ This paper is planned to appear late in the year 1949.
- ² The samples of polyethylene used were a product of E. I. du Pont de Nemours and Co., and were kindly given to the present authors by Professor H. Mark of the Brooklyn Institute of Polymer Research. The samples were optically completely isotropic before stretching. They differed strongly, therefore, from those prepared and investigated by A. Charlesby (*Proc. Phys. Soc. London* **57**, 496 (1945)). The elastomers were kindly provided by O. D. Cole of the Firestone Tire and Rubber Co., Akron, Ohio.
- ³ The concept of orientation in polythene under stress is supported by recent investigations of the infrared absorption of linearly polarized light by some of our stretched samples. These experiments were carried out by J. W. Ellis and L. Glatt in the Physics Department of the University of California, Los Angeles. According to a private communication from Professor Ellis, the spectrum features can be interpreted in terms of partially oriented CH₂ groups (see *Journal of Chemical Physics*, in press).
- ⁴ A comprehensive review of earlier investigations has been made by Wood (*J. Applied Physics* **12**, 123 (1941)).
- ⁵ Dart, Anthony and Guth, *Ind. Eng. Chem.* **34**, 1340 (1942); Dart and Guth, *J. Chem. Physics* **13**, 28 (1945).
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THE INFRARED SPECTRUM OF VULCANIZED RUBBER AND THE CHEMICAL REACTION BETWEEN RUBBER AND SULFUR *

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In an earlier paper¹ we described an infrared spectroscopic investigation of the vulcanization of rubber, and drew attention to a band at 10.4μ (960 cm.^{-1}) which appeared in the spectrum of both straight and accelerated vulcanization. We have investigated further this phenomenon, and find that the intensity of this band correlates well with the proportion of sulfur chemically incorporated, but not with the degree of vulcanization as reflected in the physical properties of the finished product.

We were unable to explain this band in a convincing manner in terms of C-S linkages, but more recently have found a band in the same position (10.4μ) and another at 11.2μ (890 cm.^{-1}) in certain thermally degraded rubbers. Since in this case the two new bands are obviously due, respectively, to the development of new CHR:CHR' and CRR':CH₂ groups, it seemed probable that the 10.4μ band might also be caused by new groupings of the former type. An investigation of the spectrum of an ebonite (in which the rubber-sulfur reaction has been carried to an extreme) confirmed this idea. In this spectrum, absorptions in the region of 6μ showed that a considerable number of bonds remained, but the characteristic absorption at 12.0μ arising from CRR':CHR'' groups in rubber had largely disappeared. On the other hand, the band at 10.4μ (although shifted to slightly longer wave lengths) had increased greatly in intensity.

These facts find a convincing explanation in the hypothesis that the reaction between rubber and sulfur causes at some stage a shift in the position of the double bond of type —CMe:CH— in the rubber chain, giving rise to a group of the type CHR:CHR. Further confirmation of this comes from the studies of Farmer and Shipley² on the reaction between sulfur and the diolefins, geraniolene and dihydromyrcene. The available data on the structures of these reaction products have led these authors to conclude that α -methylene initiation of the sulfuration reaction occurs to an important extent. They envisage attack of the $-\overset{1}{\text{CH}_2}-\overset{2}{\text{CMe}}:\overset{3}{\text{CH}}-\overset{4}{\text{CH}_2}-$ group which is common to rubber and the diolefins at the 1- and 4-positions with the initial removal of a hydrogen atom from the α -methylene carbon atoms. The radical formed by removal of a hydrogen atom from the 1-position could by resonance cause the double bond to move to the left. In this new position the double bond would still be of type CRR':CHR'', and would give rise to a radical which could move the double bond to the right and thus give rise to CHR':CHR'' groups, and hence to a band at 10.4μ in the final product.

* Reprinted from the *Journal of the Chemical Society*, December 1947, page 1699.

ACKNOWLEDGMENT

The work described above on the vulcanization and degradation of rubber will be published in more detail later. We should like to express our thanks to E. H. Farmer and R. F. Naylor for helpful discussions on the points above.

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THE MOONEY VISCOSITY AND GEL PLASTICITY RELATIONSHIP FOR GR-S-XYLENE GELS *

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This work describes an attempt to determine the extent to which plasticities of 35 per cent rubber in xylene gels vary with the Mooney viscosity (ML 4/212) of the several GR-S type of polymers used in their preparation.

No reports dealing with the correlation of Mooney number and plasticity of concentrated GR-S gels have been found, although the relationship between gel content, Mooney number, and dilute solution viscosity of GR-S and experimental polymers has been described¹.

For precise work in measuring plasticities of these viscous materials, a technique involving simultaneous mixing of the gel in a closed chamber and measurement of its plasticity was useful. This method eliminated variations due to loss of solvent, variations in the temperature of the material at the time of measurement, and the aging effect (reversible gelation)².

The instrument used in this study for measuring plasticities was a Brabender plastograph (Figure 1), consisting of a jacketed 150-cc. capacity modified sigma blade mixer, one blade rotating 60 r.p.m. and the other 90 r.p.m., powered by a constant speed motor arranged to act as a dynamometer. The counter-thrust resulting from rotation of the mixer blades within the sample is transmitted through a series of levers equivalent to one meter in length to a gram scale and an autographic recording device. Water from a constant temperature bath maintained at $25^{\circ}\text{C} \pm 0.5^{\circ}$ was circulated through the jacket of the mixer. Xylene from a dropping flask was added at a reproducible rate to the rubber in the enclosed mixing chamber through an inlet in the glass cover-plate. A 100-cc. round-bottom flask, provided with a ball-joint opening in the bottom to which capillary tubes of various diameters could be attached, was used as a dropping device. The same capillary was used in all tests. For measuring Mooney viscosity, a NBS-model Mooney viscometer was used. To determine the effect of hot and cold milling on the Mooney-plastograph relationship, samples of GR-S and GR-S-12AC were given 300 passes on both a hot and a cold mill, respectively. One part of each sample was used for the plastograph test, and the other for the Mooney determination after it had been massed in standard fashion³.

EXPERIMENTAL

Samples of rubber were cut from bales of GR-S, GR-S-10, GR-S-12AC, GR-S-50, GR-S-85, and were taken from bags of GR-S-12AC crumbs as these materials were used in one of the Chemical Corps Technical Command pilot plants. The rubber came from four different manufacturers, and represented various lots of their production. After all talced surfaces had been removed from the samples from the bales, the latter were cut into two parts; one was

* Reprinted from the *India Rubber World*, Vol. 118, No. 1, pages 66-67, April 1948.

preserved for Mooney determinations, and the other was reduced to $\frac{1}{8}$ -inch cubes by hand shears. The rubber received in crumb form had the talc almost completely removed by an air blast before the Mooney massing operation and the plastograph run. A total of 47.2 grams of the cubed or crumbed rubber was placed into the plastograph mixing chamber and moistened with a 15-cc. portion of the total amount of 87.8 grams of xylene used in making the gel. The motor was started, and at the same time the remaining xylene was poured into the dropping flask. The discharge time for the portion of the solvent run through the dropping flask was consistently between 47 and 48 minutes except in a few cases when the capillary became partially clogged with suspended matter in the reagent grade xylene used. A dropping time of even 52 minutes made no significant difference in the final readings, as was shown by subsequent check runs. The blades maintained good mixing contact with the rubber at all times.

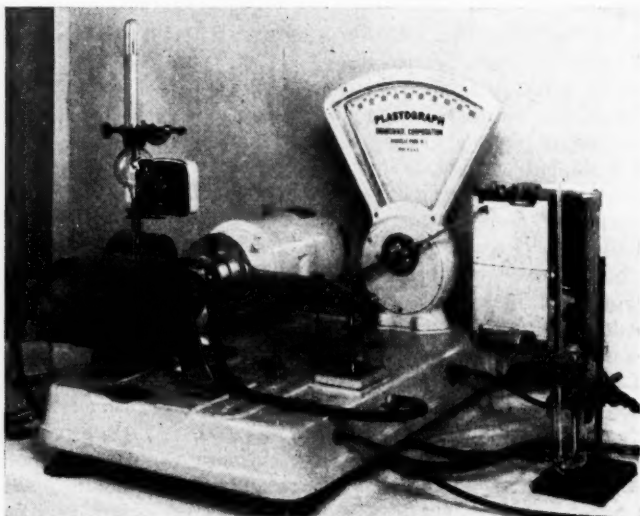


FIG. 1.—Instrument used to prepare GR-S gels and measure their plasticity showing flask used as dropping device.

The crumbed samples for Mooney number determinations were given one preliminary pass through the laboratory mill with an opening of approximately 0.015-inch to prevent slipping of the crumbs during the first few passes of the subsequent massing operation. For the milling operations, 250-gram samples of rubber were given 300 passes through the mill (opening of 0.050-inch \times 0.005) with roll temperatures of 55 to 64° F and 200 to 215° F, respectively. Duplicate samples were milled for each set of conditions (see Table 1).

CALCULATIONS

The results obtained from the determination of thirty pairs of related Mooney numbers and gel plasticities are shown in Table 2. These paired variates were used in the calculation of (1) the average variation of gel plasticity with Mooney number of the rubber (coefficient of regression); (2) the variation

in gel plasticity after its variation with the Mooney number of the rubber has been discounted (standard error of estimate); and (3) the coefficient of correlation, a number which shows how consistently the two quantities under investigation are related. The coefficient of correlation may vary from -1 to $+1$; zero shows no correlation, and 1 shows perfect correlation (see Figure 2).

TABLE 1

MOONEY NUMBERS OF SAMPLES OF MILLED POLYMER AND PLASTICITIES OF 35 PER CENT POLYMER-IN-XYLENE GELS MADE FROM THEM

Determinations Made in Duplicate for Each Set of Conditions

Polymer type	Cold Milled		Hot Milled	
	Mooney number	Gel plasticity (metergrams)	Mooney number	Gel plasticity (metergrams)
GR-S	28	92	33	110
(Original Mooney 48)	28	93	33	108
GR-S-12 AC	39	127	48	143
(Original Mooney 68)	40	131	50	137

TABLE 2

RESULTS OF THIRTY DETERMINATIONS OF MOONEY NUMBERS OF SEVERAL TYPES OF GR-S POLYMERS AND THE PLASTICITIES OF 35 PER CENT POLYMER IN XYLENE GELS MADE FROM THEM

Mooney number of polymer ML 4/212 X	Average gel plasticity (metergrams) Y
47	123
48	121
49	126
50	125
51	127
52	140
58	148
64	176
65	154
66	161
67	165
68	158
69	160
102	260
103	250
104	250

DISCUSSION

The shift from the regression line of both Mooney number and gel plasticity for the eight milled samples is interesting. If only chain scission were occurring in the mastication operations, points representing related Mooney numbers and gel plasticities of masticated samples would fall on the line or very close to it. That the points are displaced toward the ordinate indicates that, in the mild plastication studied, something is formed which influences gel plasticity more than Mooney number. It is possible that the mastication, while resulting in chain scission and consequent reduction of plasticity number, also forms polar molecular fragments which associate in concentrated xylene solution to cause a smaller drop in gel plasticity number than would be predicted from the Mooney number of the masticated GR-S.

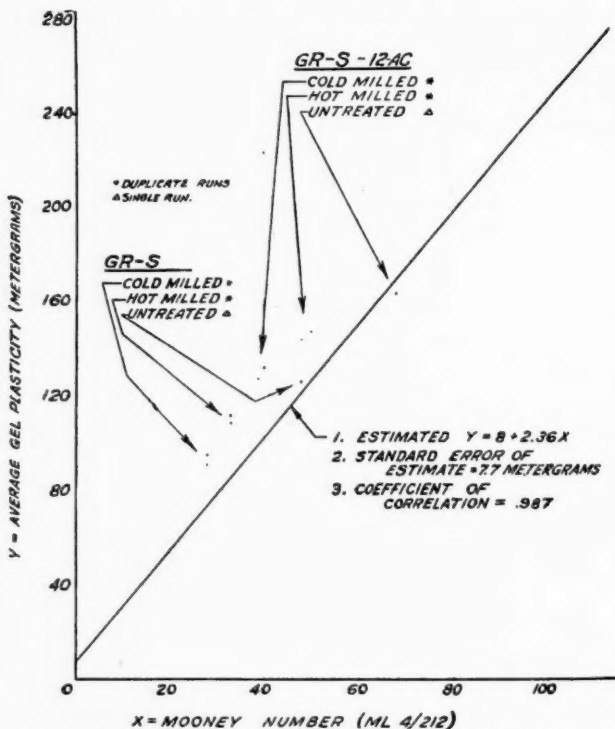


FIG. 2.—Regression of gel plasticity on Mooney viscosity of GR-S type of polymer. The effect of hot and cold milling on the polymer is also shown.

SUMMARY AND CONCLUSIONS

1. A new method for measuring plasticities of highly viscous GR-S-solvent gels is described.
2. The coefficient and the standard error of estimate for the regression of plasticities of 35 per cent GR-S-xylene gels on Mooney viscosity (ML 4/212) of the rubber have been calculated.
3. An explanation for an observed shift from the relationship established for Mooney viscosity and gel plasticity caused by hot or cold milling of the polymer is suggested.

ACKNOWLEDGMENT

The authors extend their appreciation to Ellsworth P. Cunningham, who assisted with the experimental work.

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INFLUENCE OF STRUCTURE ON POLYMER-LIQUID INTERACTION. II. INFLUENCE OF NITRILE GROUPS *

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INTRODUCTION

Swelling equilibria of a number of copolymers in various organic solvents have already been discussed¹. The influence of polarity and polarizable groups has been derived from the gradual changes of swelling equilibria. We shall deal with the same problem in the present paper, but, by considering only nitrile groups in the polymer, the resulting picture becomes less complex.

The polymers under investigation are the three series of copolymers from acrylonitrile, with butadiene, isoprene, and dimethylbutadiene, respectively. In each series, the mechanical properties change with nitrile concentration, as indicated by a gradual increase in brittleness. The combination of nitrile and methyl groups leads to a further immobilization of the flow units; the copolymers from dimethylbutadiene are, therefore, plastics at room temperature—as has been discussed in another paper².

EXPERIMENTAL

The vulcanized samples were the same as those discussed in the study of mechanical properties². It was pointed out in that article that the degree of cross-linking is not exactly the same in the three series. Copolymers from butadiene are cross-linked in the raw state, those from isoprene only to a minor degree, and those from dimethylbutadiene are still soluble. Although vulcanization leads to a certain homogenization, these differences in cross-linking can still be observed. Swelling of insoluble fractions of the raw polymers has been described in previous papers³. In most cases, vulcanization leads to a further decrease in swelling (see Table I), but occasionally it was found that the vulcanizate imbibed more liquid than the insoluble fraction of the raw polymer. This result indicates the occurrence of degradation during vulcanization. Swelling measurements were done along the same lines as before¹. Results are expressed in weight fractions.

RESULTS

The typical phenomenon of oil resistance can be observed for all copolymers (see Figure 1). Whereas polymerized butadiene swells distinctly less than the two other polymers, no influence of cross-linking or methyl groups can be observed for copolymers. The equilibrium is determined only by the number of nitrile groups in the polymer.

Swelling power increases in the series:

pentane > hexane > heptane > cyclohexane

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TABLE I
INFLUENCE OF VULCANIZATION ON THE SWELLING OF COPOLYMERS
FROM BUTADIENE

Nitrile (%)	Solvent											
	Chloroform			Carbon tetrachloride			Methyl ethyl ketone			Hexane		
	Raw	Vulc.	Diff.	Raw	Vulc.	Diff.	Raw	Vulc.	Diff.	Raw	Vulc.	Diff.
0	0.97	0.85	-0.12	0.96	0.85	-0.11	0.56	0.38	-0.18	0.92	0.55	-0.37
9.8	0.94	0.89	-0.05	0.92	0.79	-0.13	0.74	0.68	-0.06	0.34	0.24	-0.10
15.6	0.93	0.88	-0.05	0.88	0.62	-0.26	0.75	0.69	-0.06	0.12	0.12	0.00
25.6	0.92	0.86	-0.06	0.70	0.34	-0.36	0.73	0.65	-0.08	0.00	0.03	+0.03

a result in good agreement with our findings for commercial rubbers⁴.

The interaction with benzene leads to a slight maximum with 20 per cent nitrile and a distinct decrease with 50 per cent nitrile. This is the first indication of a specific interaction of nitrile groups that cannot be overcome completely by aromatics, and leads finally to the inertness of polyacrylonitrile against organic solvents.

The association of ketones diminishes with the size of substituents for two reasons: (1) the number of CO groups per volume becomes smaller, and (2)

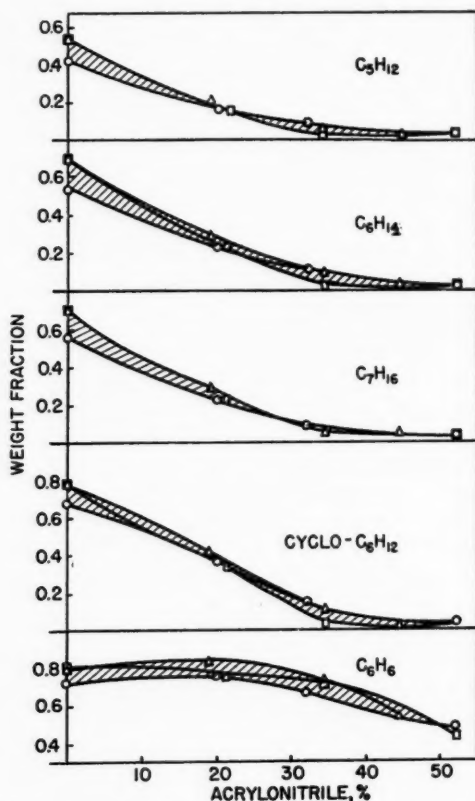


FIG. 1.—Swelling of copolymers in hydrocarbons: copolymers from butadiene (O); isoprene (Δ); and dimethylbutadiene (\square).

the bulky paraffinic groups hinder the association of the CO groups. Higher ketones, therefore, become good solvents for polymeric hydrocarbons but weak solvents for nitrile rubbers, as can be seen from Figure 2. Cyclization leads to a general increase in solvent power and, therefore, to maximum values for all

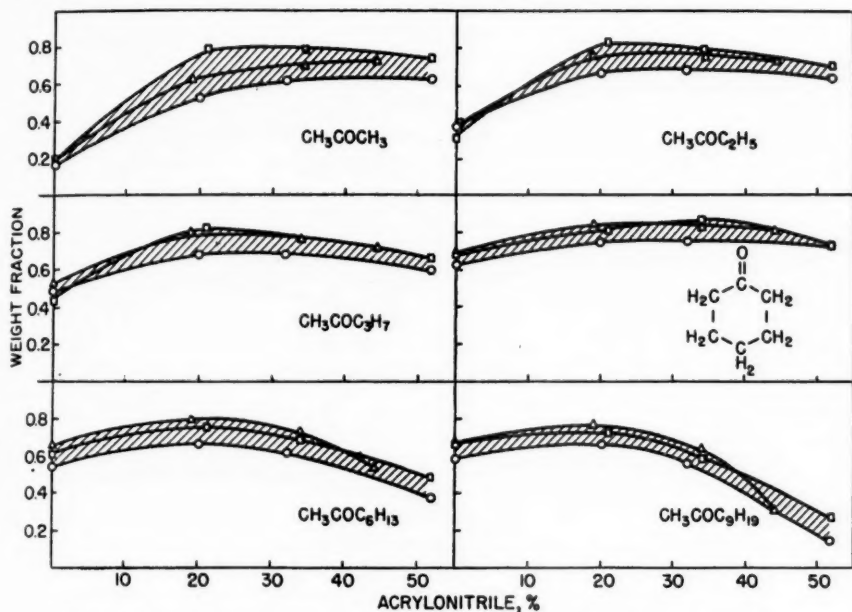


FIG. 2.—Swelling of copolymers in ketones: copolymers from butadiene (O); isoprene (Δ); and dimethylbutadiene (\square).

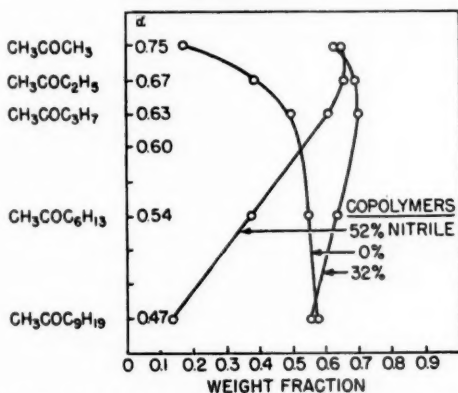


FIG. 3.—Swelling of polybutadiene and two copolymers in the series of aliphatic ketones (α , association of the solvent).

series. These correlations become even more evident from a comparison of equilibria as a function of the degree of association (α) of the solvent⁵ (see Figure 3).

The influence of a strongly polar group is illustrated by the properties of acetonitrile (b.p. 82°C) and nitromethane (b.p. 65°C), both of which interact

with nitrile rubber (see Figure 4). The association of acetonitrile indicated by its boiling point cannot be completely compensated by interaction with nitrile groups in the copolymers. The swelling equilibrium is therefore lower, as in nitromethane—a rather surprising result. The specific interaction of hydrogen bonds shows little affinity for the nitrile groups. Methyl alcohol—although more active, as with natural rubber—is still a weak swelling agent for the copolymers.

The interaction of polar groups with the copolymers is enhanced by combination with the benzene nucleus. Benzonitrile, nitrobenzene, and aniline are among the strongest solvents known for nitrile copolymers. Their interaction with the polymeric hydrocarbons, on the other hand, is indicative of the remaining degree of association in the solvent (see Figure 5).

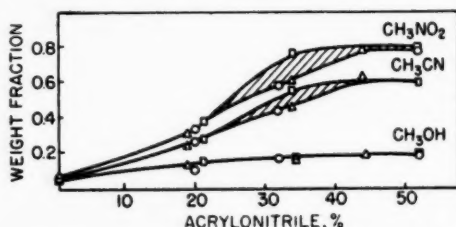


Fig. 4.—Swelling of copolymers in methanol, acetonitrile, and nitromethane.

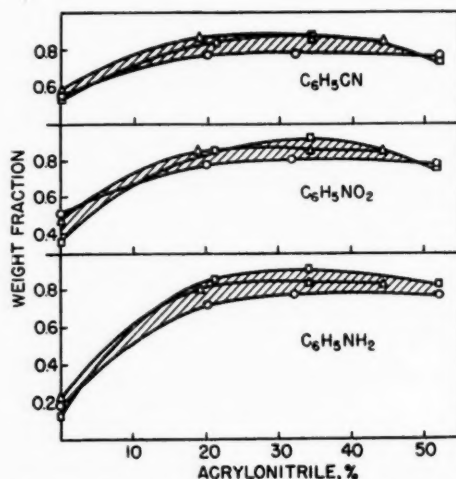


Fig. 5.—Swelling of copolymers in benzonitrile, nitrobenzene, and aniline.

The polarity of a group in combination with the benzyl group is comparable in strength with that in an aliphatic liquid. Benzyl cyanide is, therefore, a very strong solvent for nitriles and a weak one for natural rubber and allied polymers. Benzyl chloride, on the other hand, approaches the general solvent properties of chloroform (see Figure 6). Benzyl alcohol shows a surprising similarity to benzyl cyanide. It is interesting to compare these properties with the solvent power of nonaromatic alcohols of similar size. The latter are, in fact, very

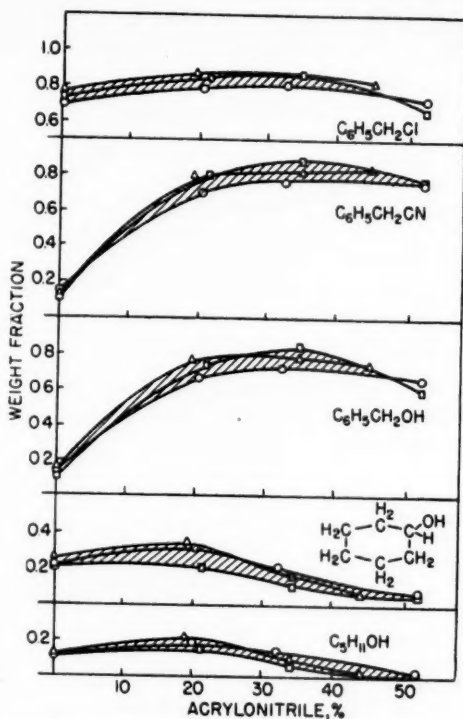


Fig. 6.—Influence of polar groups and hydrogen bonds on swelling equilibrium.

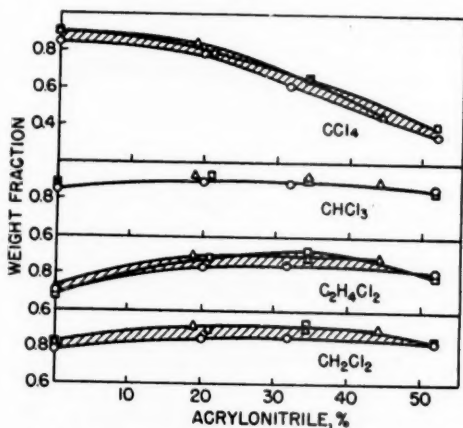


Fig. 7.—Swelling power of aliphatic chlorides.

weak swelling agents for nitriles, and interact more with polymeric olefins, thereby proving the contribution of the benzene nucleus in benzyl alcohol to the swelling action on nitriles.

Finally, we can again turn to the aliphatic halides (see Figure 7). Chloroform shows a constant solvent power over the whole range of copolymers.

Dichloromethane and dichloroethane belong to the same type, while the symmetrical carbon tetrachloride exhibits much less interaction with nitrile groups, but is still a much stronger solvent than the paraffinic hydrocarbons.

DISCUSSION OF RESULTS

It will be convenient for a general survey of our results to start from the ideal picture: a polymer swollen in a liquid of identical intermolecular forces. Such a state is approached by the swelling of Butyl rubber in cyclohexane. Here, the position of the equilibrium is determined by the degree of cross-linking in the polymer⁶. The question of how to take into account changes in intermolecular attraction now arises. Application of the van Laar-Hildebrand theory is based on assumptions which are valid only for a limited number of cases. While this theory offers the advantage of quantitative calculations⁷, it is not applicable to most of the equilibria studied in this paper. We shall also apply, therefore, the line of approach used by Langmuir⁸ twenty years ago, and shall add to it some specific assumptions derived by Staverman⁹.

According to Langmuir, miscibility can be calculated from a consideration of molecular surfaces. Various regions of such surfaces exert very different forces on their neighbors. Final equilibrium in liquid mixtures is determined by the sum of these contacts and by the shape of the molecules. Staverman introduced the concept of localized charges, which, in certain cases, are spread out over a large part of the surface, while the opposite charge is concentrated into narrow regions. By such calculations, the solvent properties of chloroform, acetone, and even benzene are fairly well understood.

The advantage of Langmuir's theory is that it makes full allowance for the occurrence of mixing with release of heat. Furthermore, it is possible to interpret the observed sensitivity of polymer-liquid equilibria¹⁰ against minute changes in composition as a consequence of alterations in molecular surface contacts. A disadvantage of the theory at present is that it does not allow a quantitative calculation of equilibria, but this is the case for all irregular mixtures of liquids.

Sometimes, it is stated that the entropy of mixing deviates little from the ideal value, even near the point of phase separation¹¹. However, such assumptions are not always valid; quite to the contrary, incomplete miscibility with water has been found to be due to an unfavorable entropy of mixing¹². Therefore, solvent-polymer interaction between molecules of unlike molecular surfaces cannot generally be treated as a system with an ideal entropy of mixing.

Our results are summarized in Figure 8 for two groups of representative polymers. The curve for polymerized dienes is practically identical with that for natural rubber, while the one with 50 per cent nitrile is an example of an extremely polar rubber. Solvents are divided into five groups: (1) paraffins, (2) weakly associated liquids of general solvent power, (3) aromatic-polar (4), aliphatic-polar, and (5) hydrogen-bonded liquids.

While the mechanical properties of the three series are influenced in a significant way by the presence of methyl groups, Figure 8 indicates only small differences for swelling equilibria when comparing polymers with the same nitrile content and different diene components. This is in good agreement with our theory that differences in mechanical properties are caused by hindered rotation of the flow units. As soon as the distances between polymer chains are enlarged by the solvent, flow units rotate freely.

We shall now discuss the change of equilibria for the two types of polymers interacting with the five types of liquids.

Polymeric olefins.—The liquid paraffins show an increase in swelling power that is in excellent agreement with the calculated increase in cohesive energy density¹³. In fact, we can see that the lower paraffins become weaker solvents. In other words, swelling equilibrium is a function of the critical temperature of the liquid. Liquefied gases such as carbon dioxide are good swelling agents for rubber, and the same can be expected to be the case for liquid propane and ethane. It can be predicted that the gradual change from a paraffin gas dissolved in rubber to a rubber swollen in the liquefied gas is governed essentially by the change in cohesive energy density of the gas in the condensed state.

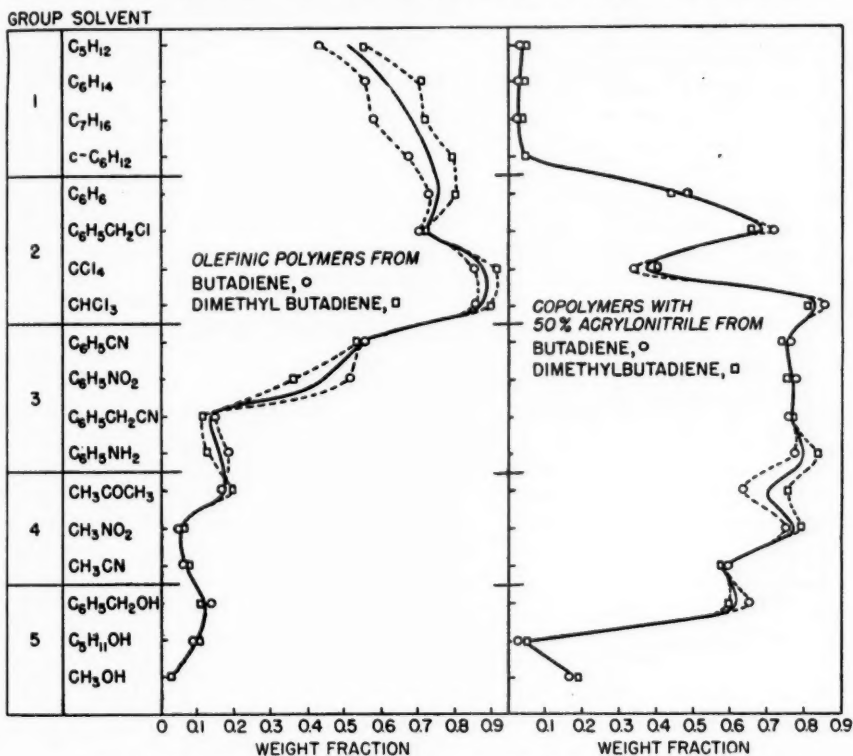


FIG. 8.—General survey of solvent power for polymeric olefins and copolymer with 50 per cent acrylonitrile.

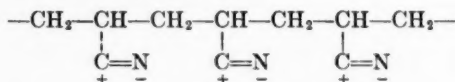
Individual differences due to cross-linking have a measurable influence on the swelling in these solvents similar to the behavior of Butyl rubber, but whereas the latter shows a maximum degree of swelling in cyclohexane and less swelling in aromatics, the situation is reversed for olefinic polymers. The van Laar-Hildebrand theory does not explain this fact, whereas an energy gain from surface contacts for the polyolefin-aromatics interaction by mutual polarization, can be made plausible. The solvent power of the second group can, therefore, be explained only in terms of the Langmuir theory. The properties of the third group (aromatic-polar solvents) are readily understood from the point of view of surface forces, while the relative change (taking benzene as an assumed standard¹³) can also be expressed in terms of cohesive energy

density, at least for nonpolar rubbers. Agreement with Gee's theory can be expected for the fourth group (aliphatic-polar, interacting with Butyl rubber), while olefinic copolymers are here a borderline case, since even a few polar groups can lead to considerable deviations from additivity. The fifth group (alcohols) is the only one in these series in which the equilibrium is easily raised by an increase in temperature. This indicates that again in energy from surface contacts can be made by reducing the degree of association in the alcohols.

Nitrile rubber.—The systems summarized in Figure 8 cannot be discussed in terms of the van Laar-Hildebrand theory¹³, but Langmuir's line of approach can be applied. The physical state of the paraffin liquids is of little importance here, since the concentration of the nitrile groups is decisive for the position of the equilibrium. Here again, we have observed an increase in swelling with temperature. The second group reveals the gain in surface energy from nitrile-benzene contact and the astonishing difference between the symmetrical carbon tetrachloride and chloroform. The third and fourth groups are distinguished by their uniform action on the polymer. It obviously does not much matter which polar groups are present as long as the concentration of paraffin residues is low. Even the hydroxyl groups of the alcohols exhibit some interaction with the nitrile groups.

This brings us finally to the other end of the scale—polyacrylonitrile.

Polyacrylonitrile.—The properties of this polymer, its hardness at 300° C, and its complete inertness against such powerful solvents as chloroform, are very different from those found for polymethyl acrylonitrile or a copolymer with as little as 10 per cent diene. In fact, they are so unexpected that a three-dimensional structure of the polymer was originally assumed¹⁴. However the discovery that strong aqueous solutions of lyotropic salts act as solvents¹⁵ revealed a sudden change in the nature of intermolecular attraction. This type of liquid-polymer interaction is comparable to that of proteins, polyamides, and cellulose. The experimental facts necessitate the assumption of hydrogen bonds and ionic forces. The occurrence of an ionic structure in hydrocyanic acid having been proposed¹⁶, the following formula for polyacrylonitrile therefore seems compatible with present theories:



The fact that methyl groups inhibit this partial ionization is probably due to two very different factors: (1) the electron-releasing properties of a methyl group within the molecule and (2) a steric screening between two chains. Polyacrylonitrile becomes hard and brittle only after drying—a change in properties quite comparable to the reversible denaturation of a protein and α -cellulose. In both cases, interpolymeric hydrogen bonds are formed between strongly polarized covalent bonds.

ACKNOWLEDGMENT

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PREPARATION AND PROPERTIES OF RUBBERLIKE HIGH POLYMERS. V. INFLUENCE OF NITRILE GROUPS ON THE PROPERTIES OF COPOLYMERS *

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INTRODUCTION

The introduction of methyl groups in butadiene leads to a decrease in 1,2- and 3,4-addition as well as to a reduction of cross-linking reactions¹. The same regularity can be observed in a series of copolymers, which will be discussed in the present paper. Apart from these interrelations between diene structure and pattern of the chain molecule, other physical properties such as the second order transition point and the closely related brittle point depend on the presence of methyl groups¹. Nitrile groups enhance these differences between the three series of diene polymers, as will be seen from the following results.

A striking contrast between these widely diverging physical and mechanical properties is the similarity of swelling equilibria, which are obviously determined only by the number of nitrile groups per volume unit of polymer, as will be discussed in another communication.

EXPERIMENTAL

Most of the copolymers used were prepared in emulsion²; those prepared in bulk³ differed only by a higher soluble fraction of the raw polymers.

Vulcanization and physical mechanical tests were done essentially along the same lines as already described¹.

RESULTS

Density.—The polymers from the three dienes show an increase in density with the number of methyl groups in the molecular unit. The same difference has been observed for the copolymers both in the raw and vulcanized state (see Figure 1). The deviation from a linear change between the specific weights of the polydiene and polyacrylonitrile (sp. gr. 1.154) is small.

The coefficient of thermal expansion between 20–45° C was found to be $5-7 \times 10^{-4}$ per degree, and almost independent of the composition of the polymer. Distinctly lower values, approximately $2-4 \times 10^{-4}$ per degree, were found between 0–20° C for some of the polymers with a high nitrile concentration.

Plasticity of raw polymers.—Measurements with the steam plastometer give a convenient qualitative picture of the raw polymers (see Figure 2). The copolymers of butadiene prepared in emulsions are sufficiently cross-linked to resist any compression on this instrument even at 100° C. The methylated

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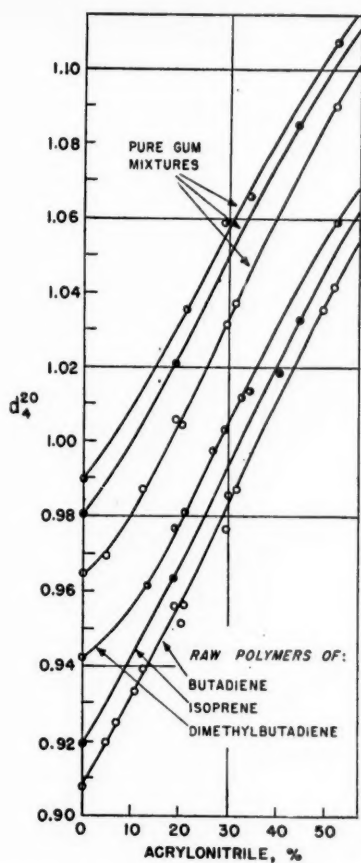


Fig. 1.—Change of d_4^{20} as a function of the nitrile concentration in copolymers, raw polymers, and vulcanized pure-gum mixtures.

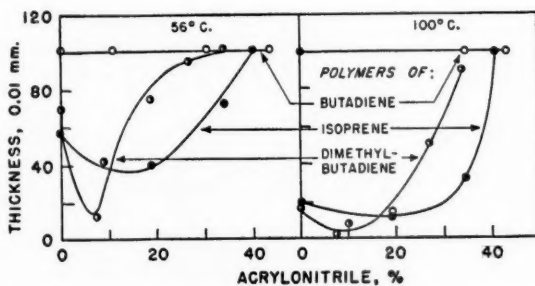


Fig. 2.—Influence of nitrile concentration on the hardness of raw copolymers measured at 56° and 100° C with the steam plastometer. The measurements give the thickness of pellets after 15 seconds' compression.

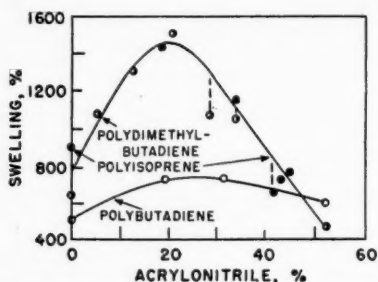


Fig. 3.—Swelling of vulcanized samples in chloroform at 20° C vs. nitrile concentration as a relative measure of the degree of cross-linking.

polymers are, on the other hand, very soft even at 56° C. Increasing quantities of nitrile groups lead to harder polymers, which, however, soften with increasing temperatures. Depending on the conditions of polymerization, the copolymers with only a small nitrile concentration are softer than methyl rubber and polyisoprene.

Cross-linking of vulcanized polymers.—A convenient measure for the degree of cross-linking produced by the vulcanization of pure-gum mixtures is the swelling in chloroform. As can be seen from Figure 3, the degree of swelling is nearly independent of the nitrile concentration, and is fairly constant in the series of vulcanized polybutadienes, while the two other series are partly under-vulcanized. By applying much longer periods of vulcanization, it was possible to prepare fully vulcanized samples. It will be clear from Figure 3 that the differences in physical and mechanical properties, which we shall now discuss, are not caused by essential differences in the degree of cross-linking.

Hardness of vulcanized polymers.—While nitrile groups cause a very gradual change in the hardness of the butadiene series, very small quantities of nitrile groups are sufficient to transform methyl rubber in a plastic material; polyisoprenes take an intermediate position, as can be seen from Figure 4.

The hard samples show the typical flow phenomenon during the measurements and soften gradually at higher temperatures. The copolymers of methyl rubber with high nitrile concentrations soften completely in boiling water.

Rate of elastic recovery.—The thermoplastic nature of the changes in physical properties are established above. The absolute value of the rate of recovery (as is well known) depends on experimental conditions, but the results reproduced in Figure 5 give a good idea of the significant relative differences in elastic properties.

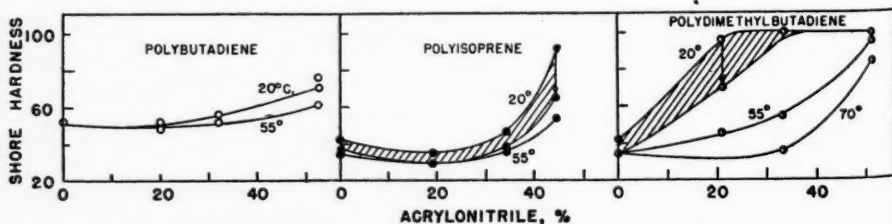


Fig. 4.—Influence of nitrile groups and temperature on the Shore hardness of copolymers.

Butadiene copolymers with 50 per cent nitrile are elastic, but retract somewhat slowly, while the corresponding products from isoprene are completely "frozen in" at 0° C and retract only slowly at 20°. The nitriles derived from methyl rubber become elastic between 80–100°; even 20 per cent nitrile is sufficient in the latter case to raise the limiting temperature of elasticity above 20°.

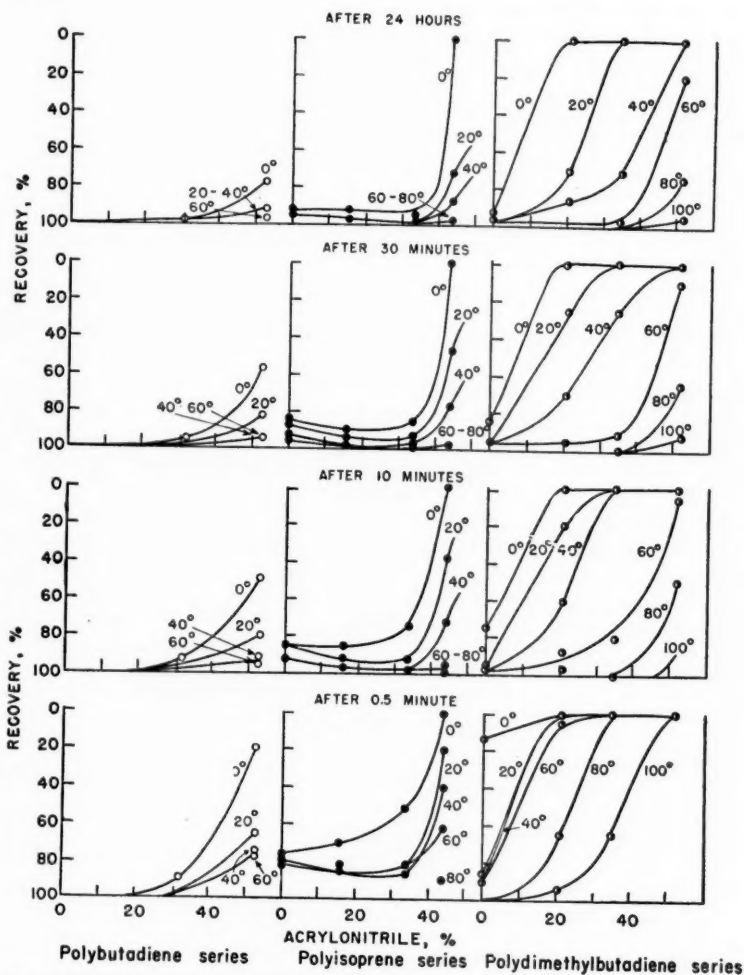


Fig. 5.—Elastic recovery of copolymers as a function of temperature and time of recovery.

Stress-strain properties.—As has been pointed out¹, regularity of the chain and structure of the molecular unit both influence the stress-strain properties of the polymers. Typical differences between the butadiene and dimethylbutadiene series can be seen from Figure 6.

Moderate quantities of nitrile groups have only a small influence on the tensile strength (at room temperature) in the copolymers of the butadiene

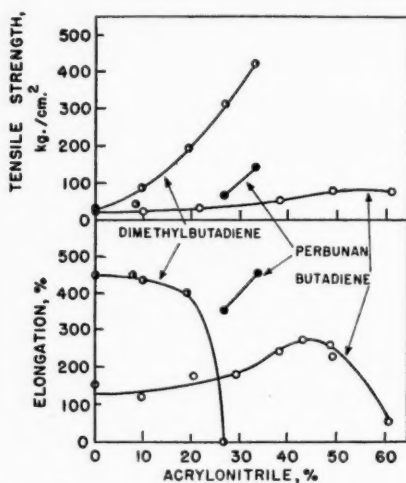


Fig. 6.—Tensile strength and elongation of dimethylbutadiene, Perbunan, and butadiene at 20° C.

series. Copolymerization leads essentially to more extensible products as the amount of cross-linking is reduced. Our preparations were somewhat inferior to Perbunan, but this influence of the method of preparation is unessential, in a comparison of the polybutadiene and methyl rubber series. These copolymers show a continuous increase in tensile strength and then a very sudden decrease in extensibility. The product with 19 per cent nitrile shows plastic flow, while with 26 per cent nitrile it is no longer extensible. These plastic properties can also be seen from the stress-strain diagram (see Figure 7). The data were obtained with a traction rate of 10 cm. in 20 seconds on a Schopper dynamometer, while with a smaller rate, *e.g.*, 10 cm. in 40 seconds, the product with 26 per cent nitrile becomes also extensible to 350 per cent.

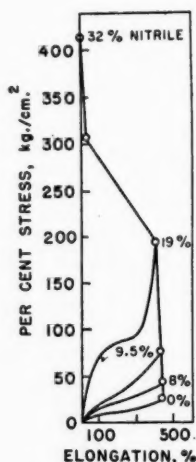


Fig. 7.—Stress-strain diagram of copolymers of dimethylbutadiene at 20° C.

Samples containing even 65 per cent nitrile are easily extensible and elastic in boiling water, and vitrify so quickly on cooling that amorphous fibers can be produced. Immersion of such a "frozen in" strip in chloroform, or even a moderate swelling agent causes contraction as soon as swelling takes place.

Brittle points.—Borders and Juve⁴ have measured the brittle points of butadiene and isoprene copolymers. Their results induced us to measure also the brittle points of the dimethylbutadiene series. Our measurements were done by hand tests on strips of the raw and vulcanized plastics. One run was performed with continuously increasing temperature, and another by cooling the material gradually below its brittle point. Small differences between individual series of the same material were encountered, and also small variations were found between material that had been shelf-aged for five years and freshly heated samples. But the regularities emerging from the combination of our results with those of the American authors are not influenced by such effects.

It can be seen from Figure 8 that the brittle point increases nearly linearly with the nitrile concentration. Thus the higher limiting temperature of elasticity in the methyl rubber series is a consequence of the high brittle point of methyl rubber.

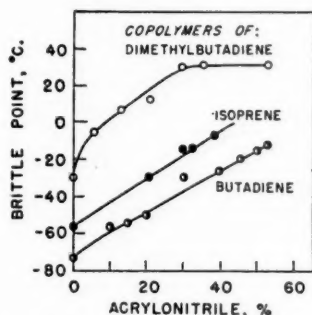


FIG. 8.—Influence of nitrile concentration on the brittle points of copolymers.

Polyacrylonitrile decomposes before softening, while a methyl group reduces the attraction between the nitrile groups sufficiently to make the polymer thermoplastic and comparable to polystyrene. Obviously, copolymerization has the same effect, since the brittle points of copolymers containing as much as 80 per cent of nitrile are still comparatively low.

DISCUSSION OF RESULTS

The main factors that determine the properties of these copolymers are the amount of nitrile and methyl groups, and the degree of cross-linking and cyclization. We believe that the influence of these factors on a number of physical properties is different and can, therefore, be determined by a qualitative comparison.

The specific gravity changes as a linear function of the two components, which indicates that the sum of van der Waals' forces is comparable to that present in a mechanical mixture of the components. All other experiments are in effect flow measurements, which reveal, therefore, more about the individual properties of flow units. The plasticity measurements on raw polymers indi-

cate the cross-linking of the butadiene derivatives, which we have already proved by measurements of the solubility². Hardness is actually measured by the degree of flow occurring under the point of a needle. We learn from Figure 4 that one type of hardness, caused by cross-linking in the polybutadiene series, depends only slightly on temperature, while the other type is thermoplastic in nature and related to a flow phenomenon. Here we find a distinct increase of plastic properties from the isoprene to the dimethylbutadiene series.

The elastic recovery is more sensitive to the composition of copolymers than other properties. The mechanical state of a 50-50 mixture of polybutadiene-acrylonitrile corresponds to that of 60-40 mixture with isoprene, while as little as 7-10 per cent acrylonitrile added to methyl rubber is sufficient to cause the same degree of stiffness.

We have already pointed out¹ that the influence of the second methyl group on the flow properties of polymers of butadiene is more pronounced than that of the first methyl group. The present experiments on elastic recovery and brittle points of copolymers give further support to this conclusion. One observation is rather typical: the change from the elastic to the "frozen in" state is very sudden in the isoprene and dimethylbutadiene series. A small increase in nitrile concentration in the presence of methyl groups is sufficient to inhibit molecular mobility. In other words, the mobility of the flow units is changing in this case with a higher power of the nitrile concentration. The changes within the series of styrene-diene copolymers, which have also been studied in these laboratories, are, on the other hand, much more gradual.

As stated earlier², the amount of cyclization is larger in the dimethylbutadiene series than in the two others. This makes it impossible at present to correlate structure and properties in a more quantitative way. In the case of natural rubber, methyl groups are all important for a number of valuable physical and technological properties, as has been discussed¹. Methyl groups in copolymers, on the other hand, contribute essentially to an undesirable rise in the limiting temperature of elasticity.

ACKNOWLEDGMENT

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MEASUREMENT OF INTERNAL DOUBLE BONDS IN POLYMERS BY PERBENZOIC ACID ADDITION *

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The double bonds in diene polymers occupy internal or terminal positions, depending on the mechanism by which the parent molecule enters the polymer chain. Thus, vinyl double bonds are formed by 1,2-polymerization of butadiene:



and internal double bonds by 1,4-polymerization:



The determination of the proportions of the two types of double bonds in natural and synthetic polymers has been attempted by isolation of the ozonolysis degradation products and by the study of infrared spectra. The ozonolysis technique has been looked upon with disfavor because of the apparent cleavage of some single bonds in addition to double linkages¹. Pale crepe, which is considered to have nearly 100 per cent internal double bonds, appears to contain 10–15 per cent vinyl double bonds following oxidative breakdown². However, successful ozonolysis studies have been reported for 50-50 butadiene-styrene copolymers³, alkali metal catalyzed polybutadiene⁴, and GR-S².

The infrared spectra of polymers provide approximate information about the proportions of 1,2- and 1,4-polymerizations⁵. The spectra of pure samples of known structure (1-octene and 2-octene), and their known mixtures are used to calibrate the instrument, but the direct application to polymer spectra involves the assumption that other structural variations are without effect on the absorption bands⁶.

The first study of perbenzoic acid addition to double bonds was made by Prileschajew⁷, but the usefulness of the reaction has been confined to the preparation of hydroxybenzoates⁸ and epoxides⁹. Other peracids—peracetic¹⁰, percamphoric¹¹, and perphthalic¹²—have been used as addition reagents in syntheses. The influence of adjacent groups on rates of addition to double bonds was of predominant interest in the early investigations.

The addition of perbenzoic acid to rubber was studied by Pummerer and coworkers¹³. The reaction was found to be rapid and quantitative, with one perbenzoic acid molecule disappearing for each double bond. Later the German synthetic rubber industry adopted the reaction to distinguish terminal and internal double bonds¹⁴. The method is based on the greater reactivity

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of internal double bonds. Presumably other addition reagents (bromine, iodine monochloride, etc.) add more rapidly to internal double bonds than to vinyl double bonds, but the reaction rates are much too fast to be used in this connection.

The German method is empirical. It defines the peracid value of a polymer as the percentage of the theoretical amount of double bonds oxidized in 2 hours (the time required to oxidize 50 per cent of the double bonds in vinyl cyclohexene under the given reaction conditions). The amount of 1,4-addition is read from a calibration curve constructed from the peracid values of compounds with known structures—styrene, vinyl cyclohexene, and 2,2-dicyclohexenyl. Separate calibration curves are required for polybutadienes and polyisoprenes because of the influence of the methyl group on the reaction rate. Thus, the German method assumes equivalent addition rates for low-molecular-weight compounds and large polymer molecules.

PERBENZOIC ACID ADDITION RATES

In the procedure for determining the amount of internal double bonds, a chloroform solution of the polymer is treated with perbenzoic acid in chloroform solvent under suitable conditions of concentration and temperature. After the time required for complete addition to the internal double bonds, an aliquot portion of the reaction solution is removed. The total amount of perbenzoic acid which has reacted is determined iodometrically, and the extent of the other means of perbenzoic acid consumption—for example, vinyl double bond reaction and side chain substitution—are subtracted in calculating the amount of 1,4-polymerization.

There are two general problems in developing an analytical procedure: (1) defining conditions for eliminating side-chain substitution reactions, and (2) separating internal and vinyl double bond contributions to the reaction. The first of these requirements was investigated by studying the effect of reaction conditions on rates of addition. The preliminary experiments are reported here in the form of rate curves for perbenzoic acid addition to the double bonds in standard specification GR-S, oleic acid and 10-undecylenic acid. The influence of reaction conditions was studied by comparison of these rate curves. Apparent double-bond saturation values larger than theoretical are indicative of side chain oxidation interference.

Pretreatment of Polymer Samples.—Small pieces of the sample were extracted with acetone for 4 hours and dried in vacuum overnight at room temperature. Samples containing gel were made soluble by milling before extraction. If insoluble material remained after the milling treatment, the polymer was dissolved in benzene and the gel filtered through a 100-mesh stainless steel screen. The soluble rubber was precipitated by methanol addition and dried in vacuum at room temperature.

Perbenzoic Acid Reagent.—Perbenzoic acid was prepared by the procedure of Braun¹⁵. If followed carefully, this method will give about a 1 *N* chloroform solution of the peracid. The solution was diluted with sufficient chloroform to reduce the concentration to 0.56–0.57 *N* and stored in a refrigerator to minimize decomposition. Under these conditions the reagent had a shelf life of at least 2 months.

Determination of Reaction Rates.—An amount of sample containing 11.1 ± 0.1 milliequivalents of double bonds was taken. This quantity is based on an assumed 100 per cent total unsaturation, and corresponds to 0.4

gram in the case of a 75/25 butadiene/styrene copolymer. The sample was dissolved in 50 cc. of chloroform, 25 cc. of the 0.56 *N* perbenzoic acid stock solution was added, and the volume was made up to 100 cc. with chloroform in a volumetric flask. All volumes were measured at $6^\circ \pm 1^\circ \text{C}$. These reactant concentrations were used in all the experiments requiring a 25 per cent excess of perbenzoic acid. Unreacted perbenzoic acid was determined by pipetting 10-cc. aliquot portions of the reaction solution into a 500-cc. Erlenmeyer flask containing 20 ml. of 10 per cent potassium iodide solution and 25 cc. of 0.4 *N* acetic acid. The iodine liberated was titrated with 0.05 *N* sodium thiosulfate. Corrections for decomposition of perbenzoic acid in the blank experiments were 1 per cent or less after 1 to 2 days at 6°C .

The techniques for determining total unsaturation of synthetic polymers do not always give unsaturation results in accord with the values calculated from theory. The interference of side chain substitution reactions is often an ex-

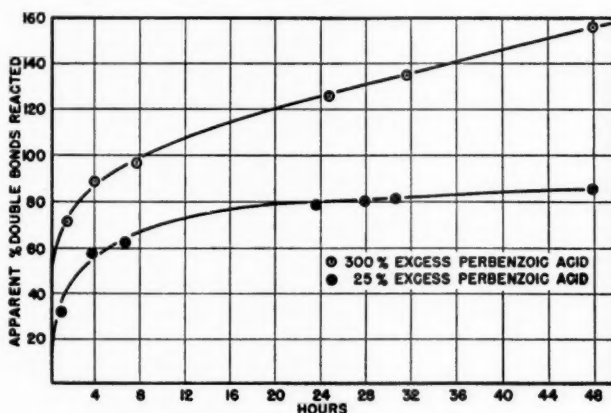


Fig. 1.—Effect of excess perbenzoic acid on rate of addition to GR-S.

planation of the difference¹⁶. As a consequence, the data that follow are on the basis of percentage internal double bonds. As the methods for determining total unsaturation are investigated further, the amount of 1,2-addition can be estimated more accurately from the difference between total unsaturation and internal double bond values.

FACTORS INFLUENCING RATE OF REACTION AND SUBSTITUTION

The two factors expected to show marked influence on the degree of substitution are percentage of excess perbenzoic acid and temperature. All the experiments described were performed, except if otherwise indicated, at $6^\circ \pm 1^\circ \text{C}$, since this was the lowest temperature (refrigerator) that could be maintained reasonably constant over long periods.

Excess Perbenzoic Acid.—Figure 1 shows the extreme effects of excess perbenzoic acid on the reaction with GR-S. Considerable substitution occurred with a large excess of reagent, while unsaturation values of the expected magnitude were obtained using a 25 per cent excess. In these two experiments a fixed weight of 0.133 gram of sample was used and the initial perbenzoic acid concentration varied.

Optimum concentration conditions were determined by studying a series of reactions using 20, 40, and 100 per cent excesses of reagent (Table I).

A 100 per cent excess provides marked evidence for side-chain oxidation. At 40 per cent excess there is a small amount of substitution, but the reaction does not carry much beyond complete oxidation of all the double bonds using a 20 per cent excess.

TABLE I
INFLUENCE OF PERCENTAGE OF EXCESS PERBENZOIC ACID ON
0.4-GRAM SAMPLE OF GR-S

Reaction time (hours)	Apparent percentage double bonds reacted		
	20% excess	40% excess	100% excess
16.5	84.8	88.2	100.0
19.0	86.4	89.1	103.9
21.0	86.8	90.7	106.3
24.0	88.1	92.7	108.3
89.0	101.0	112.7	148.3

Further justification for maintaining the perbenzoic acid concentration just above theoretical requirements became evident in oxidation studies on oleic acid and undecylenic acid (Table II).

The undecylenic acid reaction with a small excess of perbenzoic acid is second order throughout the addition. A rate constant of $0.027 \text{ mole}^{-1} \text{ min.}^{-1}$ was calculated. Presumably, addition to oleic acid is also second order, but the rate constant decreased until about 80 per cent of the reaction was complete. Then the constant was about $0.3 \text{ mole}^{-1} \text{ min.}^{-1}$.

An interesting sidelight to the study of the effect of excess perbenzoic acid is the absence of side-chain oxidation in pale crepe (natural polyisoprene) when as much as 520 per cent excess reagent was used. Complete saturation of the double bonds was accomplished within a half hour in this experiment, and no further consumption of perbenzoic acid was noted.

Solvent Medium.—Three solvents were studied—benzene, toluene, and chloroform. Benzene has the desirable property of minimizing air oxidation

TABLE II
PERBENZOIC ACID ADDITION TO KNOWN UNSATURATES

Excess of oxidizing agent (per cent) Weight sample (g.)	Oleic acid		Undecylenic acid	
	250 0.4606	20 0.5374	125 0.4706	25 0.3401
Reaction time (hours)	Apparent percentage of double bonds reacted			
2	95.2	74.6	17.8	11.8
5	100.0	82.0	37.5	20.0
10	105.0	90.2	43.9	25.0
25	113.3	98.1	80.8	49.2
45	118.1	99.5	97.0	65.2

of chloroform¹⁷, but the main objection to its use is the limited solubility of the hydrolyzed perbenzoic acid addition product. An emulsion forms which interferes with the titration. Toluene was found unsuitable because its methyl group is slowly oxidized by perbenzoic acid.

Age of Perbenzoic Acid Reagent.—An increase in oxidizing strength of aged, dilute chloroform solutions has been reported¹⁸. Evidence for this effect has

been noted during this investigation, but never any consistent trend, probably because concentrated solutions were used. The increase in titer is attributed to the air oxidation of chloroform to a peroxide compound¹⁷, perhaps catalyzed by perbenzoic acid¹⁸.

In view of this fact, the influence of the age of reagent solution was investigated. Two samples of GR-S were treated with a fresh and a 51-day-old

TABLE III
EFFECT OF REAGENT AGE ON ADDITION RATE FOR
0.4-GRAM SAMPLE OF GR-S

Reaction time (hours)	Apparent percentage of double bonds reacted	
	Fresh	Aged 51 days
17.0	85.3	84.4
19.5	86.1	85.9
21.7	87.4	86.7
23.7	87.9	87.2

chloroform solution. Nearly superimposable rate curves were obtained (Table III), which indicated the absence of any aging effects when a small excess of reagent is used.

Temperature.—Raising the temperature from 6° C to 24° C increases the reaction rate fivefold. Temperature also has a pronounced effect on the ex-

TABLE IV
EFFECT OF TEMPERATURE ON ADDITION RATE FOR
0.4-GRAM SAMPLE OF GR-S

Reaction time (hours)	Apparent percentage of double bonds reacted	
	6° C	24.0° C
5.0	72.0	87.7
24.0	88.1	104.0
30.0	89.2	108.8
49.0	93.0	115.7

tent of substitution. Side reactions are nearly eliminated at 6° C, but, as illustrated in Table IV, measured degrees of unsaturation above 100 per cent are the rule after 2 hours of reaction with 25 per cent excess perbenzoic acid at room temperature.

SEPARATION OF VINYL AND INTERNAL DOUBLE BOND CONTRIBUTION TO TOTAL REACTION

The procedure to be proposed for determining the amount of 1,4-addition is based on simple reasoning. The reaction rate curve of a polymer containing both internal and vinyl double bonds is composed of the sum of the two individual curves for the respective simultaneous second-order reactions. Since the reaction rate constants are different (by a factor of ten in the case of additions to oleic and undecylenic acid), the fast reaction of internal double bonds becomes complete at a time when only a small proportion of the vinyl double bonds have been saturated. After this period only the slow reaction need be considered. If the initial concentration of the less active reactant is small and the reaction rate is slow, then the rate curve approaches linearity. If this

reasoning applies to the case at hand, then extrapolation to zero time of the linear portion of the rate curve beyond the time for complete saturation of internal double bonds subtracts the vinyl double bond contribution to the reaction. The extrapolation technique is expected to have its limitations, since the initial vinyl double bond content cannot exceed the maximum value required for a linear extrapolation. The determination of the limiting proportion of vinyl double bonds and an illustration of the extrapolation method are considered in the next section.

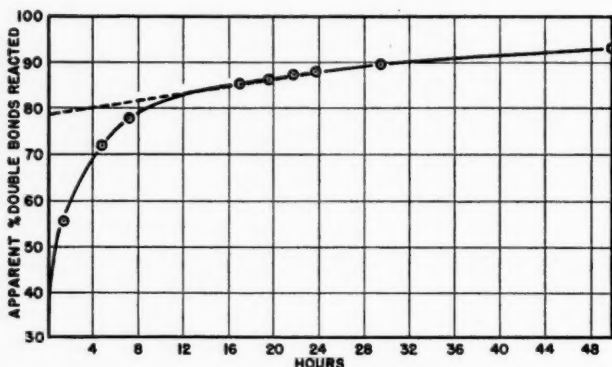


Fig. 2.—Typical rate curve for addition of perbenzoic acid to GR-S.

LIMITATIONS OF EXTRAPOLATION PROCEDURE

A typical GR-S addition rate curve, obtained under the standard conditions of 6° C and 25 per cent excess of perbenzoic acid is plotted in Figure 2. Since the internal double bonds can be expected to be saturated in about 10 hours (Figure 3, rate curve for oleic acid addition), the curve beyond this time is a measure of external double bond reaction. The 17–24 hour portion of the rate curve is most convenient to follow for routine analyses. Extrapolation of this section to zero time yields the amount of internal double bonds as the intercept. The extrapolation for GR-S is illustrated in Figure 2 and for pure oleic acid in Figure 3.

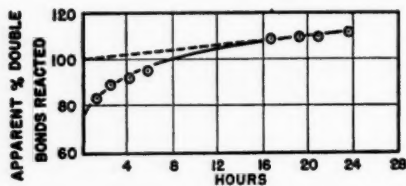


Fig. 3.—Perbenzoic acid addition to oleic acid.

The applicability range of this procedure was determined by analyzing prepared mixtures of oleic and 10-undecylenic acids. The reactions were started between 4 and 5 P.M., and three or four samples were removed for analysis at 2-hour intervals the following day. This procedure is quite convenient and suitable for routine analysis. Excellent agreement was obtained

between experimental and calculated values for oleic acid concentrations in 10-undecylenic acid mixtures containing 70 per cent or more internal double bonds (Table V). As indicated in the next section, this range of applicability

TABLE V
ANALYSES OF OLEIC-UNDECYLENIC ACID MIXTURES

Oleic acid calculated (%)	Oleic acid measured (%)	Oleic acid calculated (%)	Oleic acid measured (%)
100.0	101.0	71.7	71.5
83.2	82.5	62.1	68.0
82.9	83.0	61.0	63.0
81.9	83.1	50.7	64.0
71.9	71.0		

was found to cover most polymers with the significant exception of samples polymerized in the presence of alkali metal catalysts.

Oleic acid-10-undecylenic acid mixtures can be analyzed by the perbenzoic acid addition method with about 1 per cent accuracy. Polymer sample measurements have been duplicated with a precision of 1 per cent.

POLYMER MEASUREMENTS

A variety of polymer samples have been measured by the procedure described in the preceding section. These results are given in Table VI. Many

TABLE VI
RESULTS OF POLYMER MEASUREMENTS

Sample	Internal double bonds (per cent)
Butadiene-Styrene Copolymers	
GR-S control	78 77 77, 78
GR-S, fresh peracid	78
GR-S, peracid 51 days old	79
GR-S, A.S.T.M. acetone extraction	79
German Buna S-3, unsoftened	78, 78
German Buna S-3, heat-softened	78, 78
21.0% conversion copolymer	78
42.6% conversion copolymer	76
60.6% conversion copolymer	78
50° C acid system copolymer, pH 4.3	82, 84
10° C acid system copolymer, pH 4.5	85, 86
Miscellaneous Samples	
Acid system polyisoprene	89, 88
Alkaline emulsion polyisoprene	86
Sodium polyisoprene	59 ^a , 58 ^a
Alkaline emulsion polybutadiene	75
Alkaline emulsion polydimethylbutadiene ^b	88
Alkaline emulsion polydimethylbutadiene ^c	89
Natural Rubbers	
Pale crepe	95, 94
Smoked sheet	97
Red Congo (Landolphia)	95
Benguella (Landolphia)	97, 97
Black Congo (Funtumia)	94

^a Outside range of accuracy.

^b 0.6 part dodecanethiol modifier.

^c 0.1 part dodecanethiol modifier.

of the variables in sample pretreatment and in polymerization conditions were found to be without effect on the internal double bond measurements. Thus, in the case of the butadiene-styrene copolymer results reported in Table VI, reagent age, increasing acetone extraction beyond 4 hours, heat softening of Buna S-3, and the extent of conversion are conditions that have no influence on the proportion of 1,2- and 1,4-addition.

The internal double bond content of a polymer depends primarily on the chemical structure of the monomer. It was found that 1,4-polymerization is enhanced if the diene molecule contains a side-chain methyl group. Thus, Table VI shows that polybutadiene has 75 per cent internal double bonds, whereas polyisoprene and polydimethylbutadiene have 86-89 per cent internal double bonds.

Vinyl double-bond formation is characteristic of systems using alkali metal catalysts. Polyisoprene prepared in the presence of a sodium catalyst has considerably fewer units linked by 1,4-addition than is the case for emulsion polymers (Table VI). The infrared spectrum of sodium polyisoprene points to a high proportion of 3,4-addition¹⁹. This type of addition gives rise to isopropenyl side groups, $\text{CH}_2=\text{C}(\text{CH}_3)-$, which would be expected to add perbenzoic acid more rapidly than vinyl double bonds. Other alkali metal-catalyzed polymers such as Buna-85 and a sodium butadiene-styrene copolymer have been measured, but results are not reported here because of internal double bond contents too low (below 70 per cent) for accurate measurement by this method. These observations confirm previous conclusions based on infrared²⁰ and ozonolysis⁴ studies of polybutadiene and polyisoprene prepared in the presence of alkali metals.

Trends have been noted in the direction of higher amounts of 1,4-polymerization in low pH media in the case of butadiene-styrene copolymers and, to a smaller extent, in polyisoprene systems (Table VI). Modifier concentration does not alter the ratio of 1,2- and 1,4-addition in the case of polydimethylbutadiene (Table VI). A similar observation has been reported in butadiene-styrene copolymer studies²¹.

The highest amounts of 1,4-polymerization are to be found in natural rubbers (Table VI). All measurements on these samples were 95 ± 2 per cent.

CONCLUSIONS

Internal double bonds formed by 1,4-polymerization of diene monomers add perbenzoic acid more rapidly than do vinyl double bonds which are the products of the 1,2-type of addition. The extrapolation procedure proposed for determining internal double bond contents of diene polymers is based on this difference in addition rates. Oleic acid mixtures with 10-undecylenic acid were prepared and analyzed with an accuracy of 1 per cent. However, the method is limited to systems containing 70 per cent or more internal double bonds.

Minimum interference of side-chain oxidation by perbenzoic acid was attained by using a low temperature and a small excess of perbenzoic acid.

Methyl-substituted emulsion polymers are characterized by high amounts of 1,4-addition. Polymerizations with alkali-metal catalysts result in products of high vinyl double-bond content. A slight preference for the 1,4-type of polymerization is favored in media of low pH. Natural rubbers are formed almost completely by 1,4-polymerization.

Heat softening, modifier concentration, and extent of conversion do not influence the degree of 1,4-polymerization.

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THE DETERMINATION OF UNSATURATION IN BUTADIENE SYNTHETIC RUBBER *

P. P. KOBeko AND E. K. MOSKVINA

Up to the present time there has been no thoroughly reliable method for the determination of the unsaturation of synthetic rubber in spite of the great importance of this problem. For setting up a reliable method for the determination of unsaturation, it is necessary to show that the quantity of halogen added to the double bond is constant, and does not depend through a broad range either on the time of reaction or on the quantity of reagent added. On the other hand, in view of the indefiniteness of the structure of synthetic rubber, it would be desirable to compare by this same method the results obtained with synthetic and with natural rubber, since the structure of the latter can be studied easily, and its unsaturation can be determined precisely.

As the detailed investigations of Kemp and his coworkers¹ have shown, a well defined and accurate result is obtained for natural rubber with Wijs reagent (0.2 gram of iodine chloride solution in acetic acid). As a solvent for natural rubber Kemp used carbon disulfide, the only solvent from which rubber does not precipitate on addition of Wijs reagent.

In searching for a corresponding solvent for synthetic rubber, we tried chloroform, carbon tetrachloride, benzene, tetrachloromethane, and dichloromethane. Precipitation of synthetic rubber took place from all the solvents except dichloromethane. However, on addition of Wijs solution, natural rubber precipitated out of a solution of dichloromethane. This astonishing difference between the rubbers—the precipitation of synthetic rubber from carbon disulfide and of natural rubber from dichloromethane—prevented comparing them by the Wijs method under the same conditions.

Therefore in our work we had to use another approach, *viz.*: (1) to try to obtain well defined results with synthetic rubber, using Wijs reagent and dichloromethane as solvent; (2) to compare the unsaturation obtained for synthetic rubber and natural rubber by some sort of similar method, comparing the values for natural rubber with those obtained by the Kemp method. In addition to this, it was necessary to compare the values of unsaturation of synthetic rubber by various methods.

THE METHOD OF KEMP WITH DICHLOROMETHANE AS SOLVENT

Approximately 0.1 gram of finely cut up synthetic rubber was dissolved in 100 cc. of dichloromethane, and 25 cc. of Wijs reagent was added to the solution. The clear mixture was kept for a definite time at room temperature, after which it was titrated back to 0.1 *N* by thiosulfate solution. At the same time a control experiment was carried out, in which the reagent was added to the dichloromethane under the same conditions. The titration was carried out in glass flasks with ground glass stoppers, with vigorous shaking. The emul-

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sion formed during the agitation readily broke, and finally the titration was determined to be sufficiently clear.

Commercial dichloromethane was first treated with bromine until the color was pale red, was allowed to settle two days, was washed with sodium bicarbonate and with water, was dried over calcium chloride, and was distilled.

The following results were obtained (Table 1).

TABLE 1

Time of treatment with the agent	Unsaturation (percentage)	Average
2 hours	68.5	—
	82	
	87	
1 day [24 hours]	90.5	90.5
	90.2	
	90.8	
2 days [48 hours]	90.5	90.45
	90.4	
	90.5	
4 days [96 hours]	90.3	90.4
	90.4	
	90.1	
The solution stood overnight (18 hours)	90.4	90.35
	90.1	

With increase in concentration of Wijs solution to double the value (0.4 *N*), an unsaturation of 90.4 per cent was obtained.

As is evident from the foregoing results, the method gives values of unsaturation for synthetic rubber which, within sufficiently broad limits, do not depend on the concentration or on the time of reaction of the reagent, indicating that it gives accurate results.

COMPARISON OF THE UNSATURATION OF SYNTHETIC RUBBER AND NATURAL RUBBER UNDER THE SAME CONDITIONS

To this end we studied the conditions of the determinations of unsaturation according to the methods of McIlhenny² and of Marshall³. Approximately 0.1 gram of rubber was dissolved in chloroform. To the solution was added 0.2 *N* iodine chloride solution in carbon tetrachloride. After titrating back with thiosulfate, potassium iodate was added, and the acidity of the solution was determined by additional titration with thiosulfate. It is ordinarily assumed that this acidity is a consequence of the substitution reaction of the rubber hydrogen by halogen (from iodine chloride), with direct formation of hydrogen chloride.

With this hypothesis for obtaining the quantity of halogen added to the double bond, it is necessary to subtract double the acidity from the difference obtained between the control and the experimental solution. Introducing a correction for acidity, and using a small excess of the reagent, Pummerer and his coworkers⁴ obtained good results for natural rubber, even with a small excess of iodine chloride. The detailed investigation by Kemp showed that the calculation of this supplementary titration gives erroneous results, but that true values are obtained even when a correction for acidity is not introduced. This result he explained by the fact that acidity appears, not as the result of the replacement of hydrogen, but of hydrolysis of the rubber-halogen addition product.

Using the latter modification of the method, it became evident that, in spite of an occasional fairly good agreement of results, sharp, incomprehensible deviations were frequently encountered.

To find a reason for this, it was decided to trace the behavior of iodine chloride in the control experiment. After the first titration, potassium iodate was added both to the rubber solution and to the control flask. It appeared that the potassium iodide reveals the presence of acidity in both cases, sometimes to the same degree. Since in the control experiment the acidity cannot be the result of substitution, it obviously cannot be explained by hydrolysis of halogen derivatives of rubber in view of the absence of any acidity in the control experiment.

It was assumed, therefore, that the acidity is a consequence of the hydrolysis of the iodine chloride solution on its addition to water, both in the solution being investigated and in the control. Titration with potassium iodate represents the quantity of hydrolyzed iodine chloride, while the first titration represents the quantity of unreacted reagent. Since hydrolysis takes place in every experiment, inevitable deviations in the data result. With this hypothesis for obtaining true values of the halogen added to the rubber, it is necessary to add the number of cubic centimeters of thiosulfate consumed in the titration up to and after addition. This is done for the test solution as well as for the control. The tests confirmed this point of view. As an example, the results of one of the tests for the determination of unsaturation in natural rubber are tabulated in Table 2.

TABLE 2
SOLUTION KEPT A WEEK. PALE CREPE

Solution of thiosulfate (in cc.)								
Control test			Experimental test			Difference	Percentage unsaturation	
Up to the addition of KIO ₃	After the addition of KIO ₃	Sum	Up to the addition of KIO ₃	After the addition of KIO ₃	Sum			
119	26.8	145.8	88.0	25.8	113.9	31.9	95.5	
120.3	25.2	145.5	63.8	51.0	114.8	31	95.5	

As a verification of this hypothesis, natural rubber was selected, since it was possible to compare the data obtained for it with the increase in unsaturation determined by the Kemp method, which is known to be reliable.

TABLE 3
INVESTIGATION OF NATURAL RUBBER

Time of treatment (in hours)	Unsaturation (percentage)	Remarks
6	81	25 cc. of 0.2 N iodine chloride was added to carbon tetrachloride
12	89	
24	96.5	
48	96.6	
72	108	
Overnight (18 hours)	96.6	50 cc. of 0.2 N sol. was added
Overnight (18 hours)	96.5	

A significant number of tests were carried out, and in all instances a similar summary calculation led to close unsaturation values in spite of the deviations of individual hydrolysis values. In addition, identical values were obtained by the use of different solvents of natural rubber, including carbon tetrachloride, chloroform, dichloroethane, and tetrachloroethane.

An increase in the concentration of the added reagent to double its value did not change the unsaturation value. The dependence of the latter on the

time of standing at room temperature in the presence of the reagent is shown in Table 3.

The same experiments, carried out with synthetic rubber, gave results similar to those listed in Tables 2 and 3 for natural rubber. The unsaturation value for synthetic rubber was 90.2; in other words it coincided closely with the value obtained when Wijs reagent and dichloromethane as a solvent were used. This was convincing evidence of the accuracy of our hypothesis, and also of the possibility of the use of the method for the determination of unsaturation in natural rubber as well as in synthetic rubber. It is surprising that a similar simple solution was not found long ago, in spite of the great quantity of experimental work and theories devoted to this problem.

The results obtained make it possible to simplify the analysis significantly. The agreement of the results using Wijs solution, without calculation of the hydrolysis of iodine chloride (using a 0.2 *N* solution in acetic acid), with the results when hydrolysis is taken into account, shows that acetic acid gives protection from hydrolysis during the titration itself. In addition, acetic acid also breaks the emulsion, and greatly facilitates the determination of the end point of the titration. In view of this, experiments were carried out with a solution of 0.2 *N* iodine chloride in chloroform, with the addition of various quantities of acetic acid directly throughout the titration (Table 4).

TABLE 4

Quantity of acetic acid added throughout titration (in cc.)	Unsaturation (average value) (percentage)
5	88
10	90.4
20	90.2

Unsaturation of this type of butadiene rubber as determined by the first method (the solvent — dichloromethane, the reagent — Wijs solution) was equal to 90.2 per cent. These experiments show the accuracy of our theory concerning the protection of the solution from hydrolysis.

On the basis of the facts stated above, two methods can be proposed for the determination of the unsaturation of sodium-butadiene rubber:

(1) Dissolve about 0.1 gram of rubber in 100 cc. of dichloromethane (purified by bromine) as described above, and add to the solution 25 cc. of Wijs solution. Simultaneously add 25 cc. of Wijs solution to the control of 100 cc. of dichloromethane. Allow the solution of rubber and the control vessel with Wijs reagent to stand overnight (generally no longer than 2 days (48 hours)) and titrate back to 0.1 *N* with thiosulfate solution.

(2) Dissolved about 0.1 g. of rubber in 100 cc. of benzene (purified by the method described above) or of dichloromethane. It is possible to use, instead, other solvents not reactive with iodine chloride, *e.g.*, carbon tetrachloride, chloroform, tetrachloromethane, and so forth. Add to the solution 25 cc. of 0.2 *N* iodine chloride solution in carbon tetrachloride. At the same time prepare a control solution of 25 cc. of 0.2 *N* iodine chloride in 100 cc. of solvent. Allow the control and the solution to stand overnight. During the titration add 20 cc. of acetic acid, then titrate the liquors back to 0.1 *N* with thiosulfate solution. In both cases the unsaturation x is calculated by the formula:

$$x = k \frac{d \cdot 0.27}{a} \%$$

where d is the difference between the number of cc. of 0.1 N thiosulfate solution consumed in the titration of the control and the rubber solution, a is the weight of sample, and k is the correction factor for the titration with standard sodium thiosulfate. Apart from its simplicity, the second method is convenient in that it does not demand a specific solvent. Finally, this method can be used for a whole group of other unsaturated compounds.

SUMMARY

1. It has been found that synthetic rubber does not precipitate from a solution of dichloromethane by the addition of Wijs reagent, whereas natural rubber does precipitate under the same conditions. The reverse relation occurs with carbon disulfide as solvent.

2. A method has been developed for the determination of the unsaturation of butadiene rubber in solution in dichloromethane by the use of Wijs reagent.

3. It has been demonstrated that, by the use of a solution of iodine chloride in carbon tetrachloride, the reaction with rubber is complicated by the hydrolysis of iodine chloride during titration, but not by the substitution of hydrogen by halogen nor by the hydrolysis of the rubber-halogen addition product.

4. The possibility of obtaining accurate values for unsaturation by a calculation of this hydrolysis is demonstrated.

5. Two methods have been developed for the determination of the unsaturation of natural and butadiene rubbers.

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DETERMINATION OF UNSATURATION OF SYNTHETIC AND NATURAL RUBBERS BY MEANS OF IODINE MONOCHLORIDE *

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INTRODUCTION

A study has been made of the reaction of iodine monochloride with polymers for the purpose of developing a reliable method for the determination of unsaturation. The polymers investigated were polybutadiene and polyisoprene, and their copolymers with styrene.

Several chemical methods were tried, and iodine monochloride was found to show the greatest promise of yielding a reliable procedure. This reagent is generally applicable to the analysis of unsaturated hydrocarbons which do not contain conjugated double bonds and which react rapidly and quantitatively with iodine monochloride. High polymers present special difficulties, since the addition reaction is not always rapid and side reactions (substitution and "splitting out" of acid—see below) between the iodine monochloride and the polymer may occur during the reaction period¹. Hence an extensive investigation for each particular kind of polymer was necessary to find a procedure that would yield the correct unsaturation value of the polymer.

The experiments with iodine monochloride were based on the procedure of Kemp and Peters². In this procedure the rubber polymer, in a nonpolar organic solvent, is allowed to react with iodine monochloride, which is present in excess. The amount of iodine monochloride remaining after a reaction period of one hour at room temperature is determined by titration. It appeared that this procedure gave reproducible results with various types of polymers, but that the results did not always correspond to the true unsaturation values for the following reasons.

Kemp and Peters attempted to choose a reaction period that was long enough to allow for the complete addition of iodine monochloride, yet not long enough to allow substitution to cause an appreciable error. Unfortunately, substitution in several types of polymers is so rapid that it cannot be avoided if sufficient time is allowed for complete addition. In consequence, the results given by the Kemp and Peters procedure may be either low or high, depending on whether the reaction period is too short or too long for the particular type of polymer being analyzed. The results of the work described below indicate that the reaction period chosen by Kemp and Peters (1 hour at 25° C) leads to high results for isoprene polymers but gives fairly reliable results for butadiene polymers.

It is not possible to correct for the amount of iodine monochloride used by substitution merely by determining the amount of acid in the reaction mixture, inasmuch as there is another source of acid, the "splitting-out" reaction. The

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mechanism of this reaction is not quite clear and is discussed in the experimental part of this paper. From an analytical viewpoint it is immaterial whether the splitting-out reaction is caused by hydrohalic acid being split out by some types of addition products or by a different reaction resulting in cyclization.

An investigation of the addition of iodine monochloride, present in excess, to polymers revealed the fact that 90-95 per cent of the double bonds in the polymer add iodine monochloride within several minutes at room temperature, and that after this time the remaining double bonds react at a much slower rate. Almost all of the "splitting out" also occurs within the first few minutes of the reaction period. Consequently, any additional acid found after this time is assumed to be formed by substitution only. It will be evident that the amount of substitution after a given reaction period can be determined by subtracting the amount of acid formed in the first 10-15 minutes from the total amount of acid present in the reaction mixture. In practice, the analysis for acid is difficult because of the tendency of the acid to volatilize from the nonpolar reaction medium. Since the acid formed by splitting out and by substitution is hydriodic acid (see below), and inasmuch as hydriodic acid reacts as quickly as it is formed with excess iodine monochloride to form iodine and hydrochloric acid, it is feasible to determine the iodine in the reaction mixture instead of the acid.

Based on the above principles, a procedure was developed which yielded values of unsaturation corrected for substitution. The unsaturation values given by this procedure were found to be independent of the reaction time within wide limits. The constancy of the values provides a strong indication that the unsaturation values found are the true ones. On the basis of the experience gained in the development of this exact, but elaborate procedure, it was possible to formulate for a particular type of polymer or copolymer simpler procedures which are recommended for routine work. It should be realized that for any new type of polymer not described in this paper a routine procedure must be developed on the basis of the "exact" procedure (see Procedure I, later).

EXPERIMENTAL

POLYMERS INVESTIGATED

Emulsion-type polymers were prepared in this laboratory by polymerization at 50° C. The accompanying recipe was used for the preparation of GR-S. Emulsion polybutadiene and polyisoprene were prepared by the same recipe, except that 100 parts of butadiene or of isoprene was substituted for 75 butadiene and 25 styrene.

Ingredient	Parts by weight
Butadiene	75
Styrene	25
Ivory Soap Flakes (S. F. Flakes)	5
Water	180
Potassium persulfate	0.3
<i>n</i> -Dodecanethiol	0.5

Sodium butadiene-styrene copolymer, sodium polybutadiene, and sodium polyisoprene were obtained from C. S. Marvel of the University of Illinois; these polymers were prepared by bulk polymerization, using sodium sand as catalyst. Smoked-sheet natural rubber, Grade B, was obtained from The Firestone Tire and Rubber Company; balata (Manaos block balata) was obtained from F. T. Wall of the University of Illinois.

All samples of polymers were purified by reprecipitation (as described below) before being analyzed.

REAGENTS

Carbon disulfide.—Analytical reagent grade carbon disulfide must be used.

Chloroform.—Reagent grade should be used. The alcohol, present as an inhibitor of oxidation of the chloroform, is removed by extracting 1 liter of chloroform with three 500-cc. portions of water. The chloroform is then dried by shaking it with Dehydrite (anhydrous magnesium perchlorate). The purified chloroform must be stored in dark bottles to prevent decomposition. It should be tested for decomposition from time to time by adding a small portion to potassium iodide solution and starch. Appearance of the starch-iodine color indicates decomposition.

Iodine monochloride, 0.11 M.—This solution is prepared by adding 17.8 grams of iodine monochloride (Eastman Kodak Practical) to 1 liter of purified chloroform. The solution should be kept in the dark, and should not be used if more than one week old. The titer of this solution is determined at the time of analysis for unsaturation by preparing a blank reaction mixture and titrating an aliquot portion of it (see below).

The Eastman iodine monochloride may contain either a small amount of free iodine or of iodine trichloride. The former does not interfere if present only to the extent of a few per cent. Any iodine trichloride should be converted to iodine monochloride by addition of the proper amount of iodine to the stock solution. To test for these impurities a portion of the stock solution is added to 6 *N* hydrochloric acid and the mixture is titrated with iodate or with iodide solution, whichever is necessary to obtain the iodine monochloride end point³ (see Procedure I, later).

It should be mentioned that the melting point (27° C) of iodine monochloride is close to room temperature. If part of the iodine monochloride solidifies in the reagent bottle, it is not advisable merely to use the supernatant liquid since it contains most of the impurities (iodine or iodine trichloride), one of which is often found to be present. Quite generally, it is recommended that the bottle containing the iodine monochloride be placed in a bath of warm water until all of the solid has melted. A portion of the liquid is then used to prepare the stock solution.

If the addition product of iodine monochloride and the polymer is soluble in a mixture of carbon tetrachloride and carbon disulfide (see below), the iodine monochloride stock solution may be prepared in carbon tetrachloride (reagent grade). The stock solution in carbon tetrachloride has the advantage of being more stable than that in chloroform, and may be kept undecomposed for several months in the dark provided moisture is excluded.

Sodium thiosulfate, 0.05 and 0.1 M.—The solution is prepared by adding $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to distilled water which has been boiled, and cooled to room temperature. Carbonate or other substances, often used to prevent decomposition of thiosulfate solutions, must not be used if acid in the reaction mixture is to be determined. The solution is standardized against potassium iodate or chromate.

Potassium iodate, 0.005 M (0.02 N with respect to reduction of IO_3^- to I^-).—Reagent grade potassium iodate is dried at 110° for 1 hour, and weighed out as a primary standard.

Polymer sample.—The polymer must be purified if it contains more than about 0.2 per cent antioxidant or other impurities, or if it contains gel. The polymer is purified by reprecipitation.

Five grams of rubber is cut into small pieces and added to 500 cc. of benzene. The mixture is allowed to stand at room temperature until the rubber has dis-

solved. Usually, the sample dissolves within a day; if not, the mixture should be allowed to stand for 2-3 days. If any impurities do not dissolve, the clear solution is separated by decantation. If any gel remains it is removed from the solution by filtration through glass wool or a wire screen. The rubber is precipitated by adding the solution slowly to 2 liters of absolute ethanol containing 0.2 per cent phenyl-beta-naphthylamine (PBNA). During the addition the ethanol is stirred rapidly with a motor-driven stirrer. The rubber is separated by decantation or filtration, and washed with 100-200 cc. of 0.2 per cent PBNA solution in ethanol. The rubber is blotted with filter paper to remove excess PBNA solution, and the sample is dried. Care must be taken to prevent oxidation of the rubber during drying. If the rubber is a polybutadiene or butadiene-styrene copolymer, it can be dried safely at 80° C in a vacuum oven for 1 hour; if it is an isoprene polymer, it must be dried at room temperature; about 24 hours at a pressure of less than 10 mm. appears to be sufficient. The rubber samples should be protected from light as much as possible. If the polymer is to be obtained from a latex the same procedure may be used, except that one liter of alcohol should be used for the coagulation of about 20 cc. of latex.

RECOMMENDED PROCEDURES

Three procedures for the determination of unsaturation are described below. In Procedure I the reaction mixture is titrated after 10 minutes and after 0.5, 1, 2, and 4 hours (at 25° or at 0° C). The reaction-rate curve obtained by plotting the corrected values of unsaturation indicates the time required for complete addition; the flat portion of the curve gives the correct value of unsaturation (*e.g.*, Figures 1-3).

Procedure II is similar to Procedure I except that titrations are made after 10 minutes and after the time necessary for complete addition to the particular type of polymer being investigated (see Table II). A correction is made for the amount of substitution by determining the total amount of iodine formed and subtracting from this the amount of iodine formed by splitting out. Procedure II can be used for the types of polymers listed in Table II. A new type of polymer must be analyzed by Procedure I to find the time necessary for complete addition.

In Procedure III (the routine procedure) the polymer is allowed to react with iodine monochloride for the period of time necessary for complete addition, and then the total iodometric titer of the reaction mixture is determined by titration. The amount of substitution which has occurred during this time is assumed to be equal to the value given in Table II. This value is applied as a correction to the experimentally determined apparent unsaturation. Procedure III may give results in error by as much as 2 per cent for certain types of polymers, since the amount of substitution is not entirely reproducible.

Procedure I.—250 mg. of GR-S (or 200 mg. of polybutadiene) is weighed out and transferred to a 250-cc. volumetric flask. A tube of paper should be used as a funnel to introduce the rubber sample into the flask. Rubber does not adhere to paper but does adhere strongly to glass. If a paper funnel is not used, the rubber may stick to the wall of the neck of the volumetric flask. 50 cc. of chloroform and 135-140 cc. of carbon disulfide are added. The mixture is allowed to stand, or is gently agitated on a mechanical shaking device until the sample has dissolved (12 hours to 2 days). 50 cc. of the iodine monochloride solution is added, the mixture is immediately diluted to the mark with carbon disulfide, and mixed thoroughly.

UNSATURATION, %
10
10
10
9
9
9

GR-S
prene

After 10–15 minutes the iodine is titrated as follows: 25 cc. of the solution is pipetted into 50 ml. of 6 *N* hydrochloric acid contained in an iodine flask. The mixture is titrated with 0.2 *N* (0.005 *M*) potassium iodate solution. The end point is indicated by the disappearance of the iodine color from the organic phase. It is necessary to shake the titration mixture gently for several seconds after each addition of iodate to establish equilibrium between the two phases. If the mixture is shaken too vigorously, an emulsion forms which does not break easily.

After reaction periods of 0.5, 1, 2, and 4 hours, the reaction mixture is analyzed for total iodometric titer and for iodine. The total iodometric titer is determined in the following way: 25 cc. of the reaction mixture is pipetted into potassium iodide solution contained in an iodine flask (40 cc. of water, 10 cc. of ethanol, and about 0.5 gram of potassium iodide). The mixture is shaken, and immediately titrated with 0.05 *N* thiosulfate solution. If an emulsion forms which makes the titration difficult, more alcohol may be added. Starch solution is added near the end point. Immediately after titration with thiosulfate a separate 25-cc. portion of the reaction mixture is titrated with iodate as described above. A blank reaction mixture containing no polymer is prepared, and titrated in exactly the same way as the sample reaction mixture. Only one thiosulfate and one iodate titration of the blank need be made. These titrations may be made immediately after the preparation of the blank.

The corrected values of unsaturation are calculated from the data by means of Equation (1). The procedure for polyisoprene and its copolymers with styrene is the same as that for GR-S except that the reaction is carried out at 0° C (ice bath) instead of at room temperature. 250 mg. of the sample is taken.

The unsaturation is calculated by the equation:

$$\text{Percentage unsaturation} = \frac{[a - (b - c)] \times \text{M.W.} \times 1000}{w} \quad (1)$$

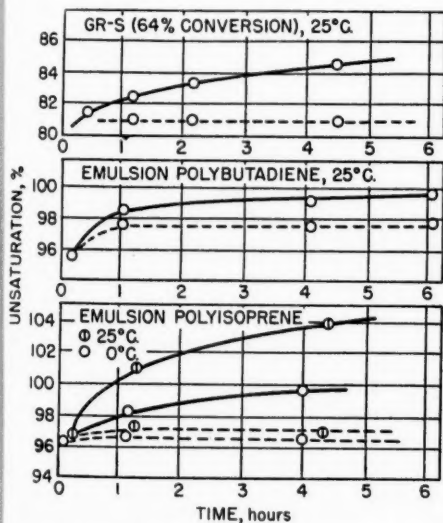


FIG. 1.—Reaction of iodine monochloride with GR-S, emulsion polybutadiene, and emulsion polyisoprene (Solid line, uncorrected; broken line, corrected.)

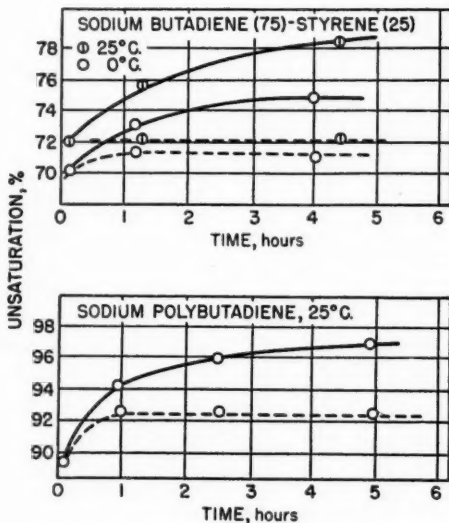


FIG. 2.—Reaction of iodine monochloride with sodium butadiene-styrene copolymer and with sodium polybutadiene.

where a is the decrease in total iodometric titer in millimoles after 0.2–4 hours; b is the number of millimoles of iodine found after 0.2–4 hours; c is the number of millimoles of iodine formed by splitting out (during the reaction period between 0 and 0.2 hour); M.W. is the molecular weight of butadiene or isoprene, 54.1 or 68.1, respectively; and w is the weight of the sample in milligrams. The unsaturation values are plotted on coordinate paper as illustrated in Figures 1–3.

As an example of the calculations involved, consider the determination of unsaturation of emulsion polyisoprene (Table I, 25° C, 1.3 hours). The amount of 0.0507 N thiosulfate used was 7.92 cc., hence the sum of the amounts of iodine monochloride and iodine in the 25-cc. portion analyzed was 0.4016 milliequivalent or 0.2008 millimole. The amount of iodine monochloride in 25 cc. of the blank was 0.5711 millimole. The value of a in Equation (1) was $0.5711 - 0.2008$ or 0.3703 millimole. The titration of free iodine in 25 cc. of the reaction mixture used 5.08 cc. of 0.0200 N (0.005 M) iodate, therefore 0.1016 milliequivalent or 0.0508 millimole of iodine was present, and b was 0.0508

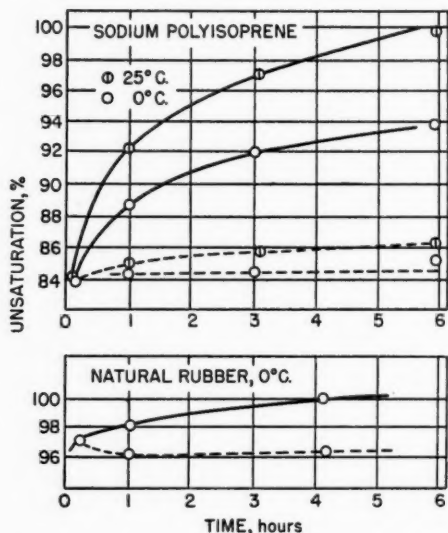


Fig. 3.—Reaction of iodine monochloride with sodium polyisoprene and with natural rubber.

(no iodine was found in the blank). The amount of iodine in the reaction mixture after 0.1 hour was 0.0375 millimole, therefore c was 0.0375. Equation (1) gives:

$$\text{Percentage unsaturation} = \frac{[0.3703 - (0.0508 - 0.0375)] \times 68.1 \times 1000}{250} = 97.3\%$$

Percentage unsaturation as calculated by Equations (1) and (2) is equivalent to the apparent percentage of polymerized butadiene or isoprene in the sample. The analytical results may also be expressed as iodine number, which is equal to 4.696 times percentage unsaturation for butadiene polymers or its copolymers with styrene, and to 3.728 times percentage unsaturation for isoprene polymers

TABLE I
REACTION OF IODINE MONOCHLORIDE WITH SEVERAL TYPES OF POLYMERS
(PROCEDURE I)

Type of polymer	Temp. (° C)	Time (hours)	Apparent unsaturation (% ^a)	Substitu- tion (^b)	Splitting out (% ^c)	Corrected unsatura- tion (% ^d)
GR-S (64% conversion)	25	0.35	81.5	0	1.6	81.5
		1.08	82.5	1.6		80.9
		2.07	83.2	2.3		80.9
		4.42	84.4	3.5		80.9
Emulsion polybuta- diene	25	0.17	95.6	0	1.0	95.6
		1.0	98.6	0.9		97.7
		4.0	99.3	1.6		97.7
		6.0	100.0	1.9		98.1
Emulsion polyisoprene	0	0.1	96.3	0	8.7	96.3
		1.2	98.2	1.4		96.8
		4.0	99.8	3.0		96.8
	25	0.1	96.6	0	10.7	96.6
		1.3	101.1	3.8		97.3
		4.3	104.0	6.7		97.3
Sodium butadiene (75)- styrene (25)	0	0.17	70.2	0	7.2	70.2
		1.2	73.0	1.5		71.5
		4.0	74.9	3.9		71.0
	25	0.10	72.1	0	7.0	72.1
		1.3	75.5	3.4		72.1
		4.4	78.6	6.2		72.4
Sodium polybuta- diene	25	0.15	88.8	0	5.2	88.8
		1.0	93.8	1.7		92.1
		2.6	95.6	3.4		92.2
		5.0	96.5	4.6		91.9
Sodium polyiso- prene	0	0.17	83.9	0	25.0	83.9
		1.0	88.9	4.4		84.5
		3.0	92.3	7.7		84.6
		6.0	94.0	8.4		85.6
	25	0.10	84.1	0	30.5	84.1
		1.0	92.5	7.4		85.1
Natural rubber	0	3.1	97.5	11.6	1.1	85.9
		6.0	100.0	13.2		86.8
		0.17	97.8	0		97.8
		1.0	98.4	1.7		96.7
		4.2	99.9	3.4		96.5

^a Not corrected for substitution.

^b Substitution is expressed as mole-per cent of iodine formed in the reaction mixture after 0.2 hour and is calculated from the equation:

$$\text{Percentage substitution} = \frac{(b - c) \times \text{M.W.}}{w} \times 1000$$

where the symbols are defined as in Procedure I above.

^c Splitting out is expressed as mole-per cent of iodine formed during the reaction period 0-0.2 hour and is calculated by the equation:

$$\text{Percentage splitting out} = \frac{c \times \text{M.W.}}{w} \times 1000$$

^d Corrected unsaturation is calculated by Equation (1).

or its copolymers with styrene. The expression in percentage unsaturation is usually more convenient than in iodine number, because (1) it represents directly the percentage of theoretical unsaturation of polymers prepared from only one monomer, and (2) it gives the weight-per cent of butadiene in copolymers prepared from butadiene and styrene, provided these copolymers have the theoretical unsaturation. The same is true for copolymers of isoprene and styrene or other monoolefins. For copolymers of two dienes, like butadiene and isoprene, the expression as iodine number is indicated.

Procedure II.—This procedure is identical with Procedure I except that aliquot portions of the reaction mixture are titrated after 10 minutes and after the time required for complete addition, as specified in Table II. The unsaturation of the sample is calculated by Equation (1).

Procedure III.—100 mg. of GR-S or polyisoprene, or 80 mg. of polybutadiene is weighed into a 300-cc. iodine flask. 20 cc. of chloroform and 60 cc. of carbon disulfide are added. The mixture is allowed to stand or is agitated gently until the sample has dissolved. 20 cc. of the iodine monochloride solution is added at the reaction temperature recommended in Procedure I. The reaction mixture is allowed to stand for the period of time specified in Table II, and then 50 cc. of water containing 0.5 gram of potassium iodide is added. The mixture is shaken and titrated with 0.1 *N* sodium thiosulfate solution. Starch is added near the end point. A blank, containing no polymer, is prepared and titrated in the same way as is the sample solution.

The unsaturation of the polymer is given by Equation (2):

$$\text{Percentage unsaturation} = \left[\frac{a \times \text{M.W.} \times 100}{w} \right] - d \quad (2)$$

where *d* is the correction for substitution given in Table II and the other symbols are the same as in Equation (1).

DISCUSSION OF ANALYTICAL METHODS

The determination of the total iodometric titer is simple and accurate. It has been found experimentally that appreciable hydrolysis of the polymer addition product or splitting out does not occur during the titration, provided this operation is carried out within 3–5 minutes.

The titration of iodine³ should also be carried out rapidly. It is accurate to about 0.05 cc. of 0.02 *N* iodate solution. The iodine monochloride may contain a small amount of free iodine. This amount of iodine will be found in the titration of the blank. For the purpose of calculating the value of unsaturation no account need be taken of this iodine, since both *b* and *c* in Equation (1) include it. However, if it is desired to find the amount of splitting out for a given polymer, the iodine found after 0.2 hour must be corrected for the amount of iodine in the blank.

If, for purposes of research, it is desired to find the amount of acid in the reaction mixture, this is done conveniently by the iodometric method of McIlhiney⁴. A 50-cc. portion of the reaction mixture is added to aqueous iodide solution and titrated with thiosulfate as described in Procedure I. The titrated mixture is then poured into a separatory funnel, and the organic layer is removed and discarded. About 50 mg. of potassium iodate is added to the aqueous layer. The mixture is allowed to stand for 15 minutes and then titrated with the thiosulfate solution.

Ordinary distilled water often contains traces of ammonia which interfere with the determination of acid. The amount of ammonia can be estimated with Nessler's reagent or in other ways. If the water is more than about 2×10^{-5} *M* in ammonia, the ammonia should be removed by distillation from an acid medium.

It will be observed that in this procedure the aqueous mixture after addition of iodate must be allowed to stand so that the reaction of iodate with acid and iodide can go to completion even when traces of acid are present. To prevent the hydrolysis of polymer addition product, it is necessary to separate the phases.

In regard to the determination of acid it must be realized that hydrochloric acid is not very soluble in nonpolar solvents and that precautions must be taken to prevent its loss. As an example of the errors caused by volatilization, a 0.002 *M* hydrochloric acid solution in 60 carbon disulfide-40 chloroform has been found to lose acid by volatilization at a rate of about 10 per cent per day, the mixture being contained in a volumetric flask with an ordinary, snug-fitting glass stopper. The loss of acid during a reaction period of a few hours does not cause an appreciable error if the flask is tightly stoppered and if, during transfer of the reaction mixture for analysis, the tip of the pipet is immersed in the aqueous solution. For longer periods, the stoppered reaction flask can be inverted over a cup of mercury. The seal thus formed completely prevents loss of acid.

EXPERIMENTAL RESULTS

Before considering the nature of the splitting out reaction and of substitution it is of advantage to consider the extent to which these reactions take place with several different types of polymers. The necessary information is found in Table I and Figures 1-3, in which are given the data from the analyses of polymers by Procedure I.

It is evident from Figures 1-3 that the substitution after a reaction period of one hour at 25° C is of the order of 1 per cent for emulsion butadiene and butadiene-styrene polymers, 2 per cent for the corresponding sodium polymers, 3 per cent for emulsion polyisoprene, and 7 per cent for sodium polyisoprene (see footnote *b* to Table I for definition of percentage substitution). It is evident that substitution can be neglected without causing a large error in the analysis of some types of polymers, but cannot be neglected in the analysis of others.

The amount of splitting out is also quite different for different types of polymers. At 25° C it is about 1 per cent for emulsion polybutadiene and butadiene-styrene copolymer; and about 10 per cent for emulsion polyisoprene (see footnote *c* to Table I for definition of percentage splitting out). The splitting out is considerably larger for the corresponding sodium polymer, amounting to about 6 per cent for the polybutadiene and butadiene-styrene copolymer and 30 per cent for the polyisoprene. The splitting out in the case of natural rubber is relatively small, about 1 per cent at 0° C.

TABLE II

CONDITIONS FOR DETERMINATION OF UNSATURATION BY THE ROUTINE PROCEDURE

Polymer	Temperature (° C)	Time needed for complete addition (hr.)	Approximate substitution (%) ^a
Emulsion butadiene-styrene (GR-S)	25	1.0 ^b	1.2
Emulsion polybutadiene	25	1.0	1.0
Emulsion polyisoprene	25	0.2	1.0
	0	0.4	1.0
Sodium butadiene-styrene (75-25)	25	1.0 ^b	2.3
Sodium polybutadiene	25	1.0	1.7
Sodium polyisoprene	25	0.2	2.8
	0	0.4	2.5

^a Expressed as mole-per cent of total number of double bonds (see Table I) so that the value given can be applied as a correction to the apparent unsaturation determined by Procedure III.

^b Complete within 0.5-1 hour.

It can also be seen from Figures 1, 2 and 3 that the addition of iodine monochloride to some types of polymers is faster than to others. The isoprene polymers react more rapidly than butadiene polymers. It also appears that the butadiene-styrene copolymers react more rapidly than the butadiene polymers; at present there is no theoretical interpretation of this result.

For routine analysis of polymers, where it is desirable to titrate each sample only once, the data in Table I can be used to establish a period of reaction in which the addition is practically complete with each type of polymer and to provide an approximate correction for the substitution which occurs during this period. This information is given in Table II and is to be used in conjunction with the routine Procedure I.

Table I shows that emulsion polybutadiene and polyisoprene have 97-98 per cent of the theoretical unsaturation (one double bond per monomer unit). Apparently, a cyclization reaction occurred to a slight extent during polymerization and resulted in the loss of 2-3 per cent of the amount of double bonds theoretically expected in the polymer.

Samples of GR-S of different conversions were analyzed by Procedure I, and were found to have nearly the theoretical unsaturation calculated from the

TABLE III
UNSATURATION OF GR-S AT DIFFERENT CONVERSIONS

Conversion (%)	Unsaturation by Procedure I (%)	Styrene content by ICI method ^a (%)	Styrene content by spectrophotometric method ^a (%) ^b
21	82.5	17.5	17.6
41	81.1	18.9	18.4
64	80.9	19.1	20.0
77	80.5	19.5	20.7

^a Calculated from the relation: styrene content = 100 - percentage unsaturation.

spectrophotometrically determined styrene content. (The polymers were prepared as described in the experimental part. The polymerizations were carried out at 50° C for different lengths of time.) Thus, the experimental unsaturation can be used to calculate the styrene content. In Table III the styrene content calculated in this way is compared with that obtained by the spectrophotometric method. The two methods give results which agree to within about 1 per cent.

Unsaturation of the sodium polymers was considerably less than theoretical. The unsaturation of sodium polybutadiene was 92 per cent of the theoretical value, and that of sodium polyisoprene was 85 per cent. The sodium copolymer of butadiene (75)-styrene (25) also had an unsaturation considerably less than the theoretical value. Since the styrene content of this copolymer was not determined, the theoretical unsaturation was not known.

DISCUSSION OF ADDITION SPLITTING OUT AND SUBSTITUTION REACTIONS

ADDITION REACTION

The addition of iodine monochloride to an unsaturated polymer leads to a halogenated product in which iodine and chlorine atoms are attached to adjacent carbon atoms. It is known that a reaction such as the following⁶ does

not occur with rubber polymers:



Evidence for this statement was obtained by titrating the iodine and acid formed in the reactions of iodine monochloride with several types of polymers. It was found in every experiment that the molar amount of iodine was equal to the molar amount of acid. It must be concluded that the only sources of iodine were substitution and splitting out and that the above reaction did not occur.

In studies carried out by C. W. Carr several years ago in this laboratory, an attempt was made to develop a gravimetric method for determination of unsaturation. The iodine monochloride addition product of GR-S was precipitated quantitatively by addition of ethanol to the reaction mixture. This method was found to give approximately correct results. However, errors were caused by splitting out and by substitution reactions, the former tending to lead to low results and the latter to high results. For this reason the gravimetric procedure was abandoned in favor of the volumetric method.

In the analysis for unsaturation it would be of advantage to find a catalyst which would increase the rate of addition without affecting the rate of substitution. There is evidence that the addition is a molecular or ionic reaction, perhaps similar to the addition of bromine in a polar solvent to ethylenic bonds⁷. A free radical mechanism, such as occurs in the addition of chlorine in carbon tetrachloride to natural rubber⁸, is unlikely in view of the fact that neither peroxides, which often promote radical reactions, nor iodine, which often retards radical reactions, was found to affect the rate of addition to an appreciable extent. Neither tin tetrachloride nor mercuric acetate, each present at 1 per cent of the concentration of iodine monochloride, was found to affect appreciably the rate of addition. It should be pointed out that these experiments were carried out using a nonpolar solvent, 60 carbon disulfide-40 chloroform, and that the conclusions do not necessarily apply to the addition in a polar solvent. It has been observed that the addition of iodine monochloride to polymers and other substances containing ethylenic bonds is slower in chloroform-acetic acid solutions than in chloroform-carbon tetrachloride solutions⁹.

The dependence of the rate of addition on the structure of the molecule in the vicinity of the ethylenic bond is an important factor in determining unsaturation. It has been demonstrated that the addition of bromine to double bonds is expedited if an electron releasing group, such as an alkyl group, is attached to one of the carbon atoms of the double bond, the reaction being carried out in a nonpolar solvent¹⁰. An electron attracting group, such as a halogen atom, attached to one of the carbon atoms of the ethylenic bond, retards the addition. A similar behavior was found with iodine monochloride under the conditions of Procedure I. Polyisoprene reacted more rapidly than polybutadiene, and polybutadiene more rapidly than polychloroprene (Neoprene). The reaction of the latter was very slow.

The rates of addition of iodine monochloride to several compounds under conditions of Procedure I are given in Table IV. The addition to oleic acid is faster than that to undecylenic acid, as would be expected from the fact that an alkyl group tends to release electrons more readily than does a hydrogen atom. For the same reason the rate of addition of iodine monochloride to bonds formed by 1,4-addition (internal double bonds) would be expected to be about 2-4 times as fast as the rate of addition to bonds formed by 1,2-addition

TABLE IV
RATE OF ADDITION OF IODINE MONOCHLORIDE TO DOUBLE BONDS^a

Compound	Type of double bond	Approximate second order rate constant ($M^{-1} \text{ sec.}^{-1}$)	Time required for 99% reaction under conditions of Procedure I (minutes ^b)
Oleic acid	$-\text{CH}=\text{CH}-$	35	0.2
Undecylenic acid	$-\text{CH}=\text{CH}_2$	11	0.7
Second double bond in linoleic acid	$\begin{array}{c} \text{Cl} \quad \text{I} \\ \quad \\ -\text{CH}-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}- \end{array}$	4.4	1.8

^a The data were obtained by allowing the compounds to react with iodine monochloride in 90 CS_2 -10 CCl_4 . The initial concentrations were: iodine monochloride 0.013 M , double bonds 0.010 M . Reaction carried out at room temperature in the dark.

^b Calculated from the second order rate constant using the initial concentrations prevailing in Procedure I.

(external). Thus, sodium polymers that contain a much larger portion of external double bonds than do emulsion polymers¹¹ would be expected to react at a somewhat slower rate. The presence of styrene in a copolymer would not be expected to affect the rate of addition appreciably since the phenyl groups are separated from the double bonds by two or more carbon atoms (not including carbon atoms attached to double bonds).

The addition to the first double bond in linoleic acid is about as rapid as to oleic acid (Table IV). Addition to the second double bond is retarded to some extent by the presence of the electron-attracting halogen atom attached to the chain two carbon atoms distant. It is seen that under the conditions of Procedure I, even the addition to linoleic acid is essentially complete within 2-3 minutes at room temperature. It should be mentioned that addition to one double bond in a compound containing two conjugated ethylenic bonds is rapid, but that the addition to the second double bond is very slow unless a large excess of iodine monochloride is present¹².

Inasmuch as the double bonds in rubber polymers are separated by at least two carbon atoms (not including the carbon atoms attached to the double

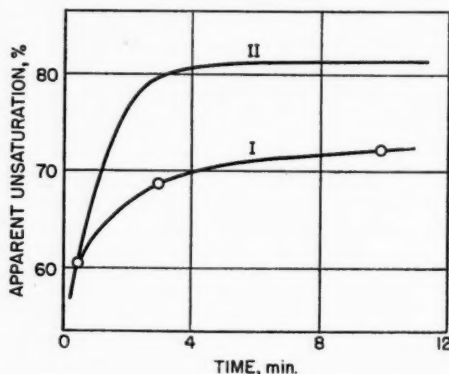


FIG. 4.—Rate of reaction of iodine monochloride with GR-S (experimental conditions, the same as those described in Table IV; unsaturation of GR-S, 81 per cent): curve I, experimental; II, theoretical curve calculated from the second-order rate constant given by the experimental point at 0.5 minute.

bonds) it might be expected that iodine monochloride would add to polybutadiene or GR-S at a rate between that for linoleic acid and that for oleic acid. Quite a different result is found experimentally, as shown by Figure 4. It is seen that GR-S reacts rapidly during the first few minutes with a rate comparable to that of oleic or undecylenic acid. This would be expected from the considerations above. However, the reaction soon becomes sluggish and the remaining double bonds react very slowly. The reason for this is not known, the effect being too large to be attributable to the presence of added iodine monochloride or to the presence of external double bonds. It seems that some bonds in the GR-S and other polymers are sterically less accessible than others.

SPLITTING-OUT REACTION

The formation of acid by splitting out has been investigated by Buckwalter and Wagner¹³. They established definitely that the addition of bromine to ethylenic compounds, such as oleic and undecylenic acids, in carbon tetrachloride was followed by the splitting out of hydrobromic acid. It has been suggested by others that splitting out also occurs when iodine monochloride reacts with rubber polymers.

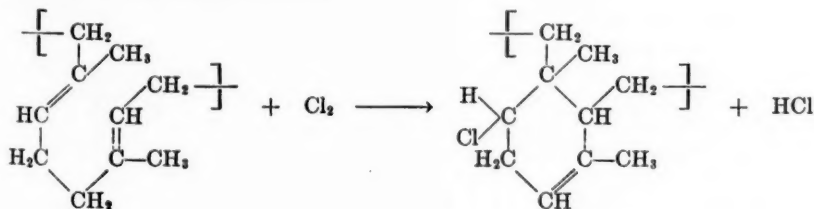


The new double bond created by the splitting out does not react further with iodine monochloride, presumably because of the inhibitory inductive effect of the halogen remaining in the polymer (see above).

It is known from experimental evidence that hydriodic acid is formed in the reaction mixture and that the source of this acid cannot be substitution alone. The evidence is: (1) if the acid is assumed to result from substitution alone, the corrected value of unsaturation of polymers is lower than the theoretical unsaturation, in some cases by as much as 30 per cent; (2) it is found that acid is formed within the first few minutes of the reaction period, during which time the amount of substitution would be expected to be negligible.

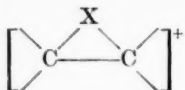
If splitting out does occur, it is necessary to assume that only certain types of double bonds are capable of splitting out and that hydriodic acid is split out from these immediately after addition has taken place. The different types of double bonds represent different structural configurations of the polymer chain in the vicinity of the bond.

On the basis of the work of Bloomfield¹⁴ on the reaction of chlorine with natural rubber in carbon tetrachloride it appears, in this instance, that splitting out does not occur, but rather a cyclization which leads to the same analytical results as does splitting out (namely, one molecule of halogen and one effective double bond disappear, and one molecule of acid appears). The cyclization reaction is represented as follows:



As a result of this reaction one of the two double bonds in two isoprene units disappears and a six-membered ring is formed in the polymer chain. The remaining double bond is quite reactive and adds chlorine readily.

Cyclization may also occur during the reaction of iodine monochloride with rubber molecules¹⁵, in which case the cyclization reaction would compete with addition. Indeed, it is possible that the active intermediate of the cyclization reaction is identical with the active intermediate of the addition reaction:



where X is a halogen atom. The intermediate ion can react with a halide ion⁹ or halogen molecule, leading to normal addition, or it can react with a carbon atom in the polymer chain, leading to cyclization.

The reaction which accompanies the addition of iodine monochloride to polymers frequently has been assumed to be splitting out, and is named so in this paper for convenience. However, the following experimental results indicate that the reaction is actually cyclization:

(1) No acid was formed in the early stages of reaction of iodine monochloride with the olefinic compounds listed in Table V. These compounds

TABLE V
SPLITTING OUT OF ACID FROM POLYMERS AND COMPOUNDS (PROCEDURE I)

Polymer or compound ^a	Temp. (° C)	Amount of splitting out	
		with ICl (%)	with Br ₂ (%)
Emulsion butadiene-styrene (GR-S)	25	1.6	6
Emulsion polybutadiene	25	1.0	
Emulsion polyisoprene	0	8.7	
	25	10.7	
Sodium butadiene-styrene	0	7.2	
	25	7.0	
Sodium polybutadiene	25	5.2	
Sodium polyisoprene	0	25.0	
	25	30.5	64
Natural rubber (<i>cis</i>)	0	1.1	29
Balata (<i>trans</i>)	25	6	
Oleic acid	25	0	0
Undecylenic acid	25	2	0
Styrene	25	0	0

^a The following compounds gave no splitting out, or less than 2%, with iodine monochloride at room temperature: isobutylene, 1,4-pentadiene, 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene, myrcene.

represent a number of different types of double bonds, and if the acid-forming reaction were splitting out, some of them might be expected to yield acid. On the other hand, if the acid-forming reaction were cyclization, none of these compounds would yield acid.

(2) If splitting out were the acid-forming reaction, it would be expected that iodine monochloride would add slowly to the newly created double bonds and that the value of unsaturation, corrected for substitution, would increase over a long period of time. Experimentally, it was found that the corrected values of unsaturation of sodium polyisoprene, GR-S, and natural rubber did not increase over a period of one week at room temperature. Iodine monochloride was also allowed to react with Neoprene over the same period of time.

In Neoprene a halogen atom is attached to one of the carbon atoms of each double bond, and therefore the double bonds would be expected to be similar to those created by splitting out. The addition to Neoprene proceeded to a considerable extent in one week, showing that iodine monochloride does add slowly to the type of double bond which would be formed by splitting out.

In the proposed method for determination of unsaturation it is not necessary that the amount of acid formed by splitting out in the reaction of a given polymer with iodine monochloride be reproducible from one experiment to the next, inasmuch as aliquot portions are taken from a single reaction mixture for analysis (Procedures I and II). However, if conditions could be found under which the splitting out would be reproducible and constant, the experimental procedure for determination of unsaturation could be simplified. Actually, it was found that the splitting out was reproducible if the same batches of reagents were used, and if the reactions were carried out simultaneously. Thus, the acid formed by splitting out from sodium polyisoprene in four experiments (Procedure I, 25° C) carried out simultaneously was found to be 23.8, 23.2, 24.5, and 24.4 per cent, respectively. On the other hand the splitting out from the same sample of sodium polyisoprene treated according to the same procedure was found to vary in an irregular manner from 23 to 40 per cent over a period of several months. It should be added that fresh samples of the polymer were prepared from time to time by reprecipitation of a quantity of the stock supply, which contained inhibitor. It does not seem likely that peroxides present in the samples could cause the observed irreproducibility.

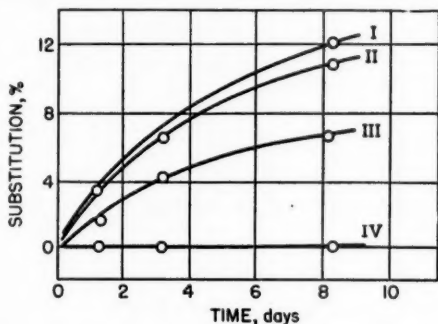


FIG. 5.—Rate of substitution of iodine monochloride in several compounds (temperature, 30° C; in the dark): I, oleic acid; II, octane; III, undecylenic acid; IV, styrene.

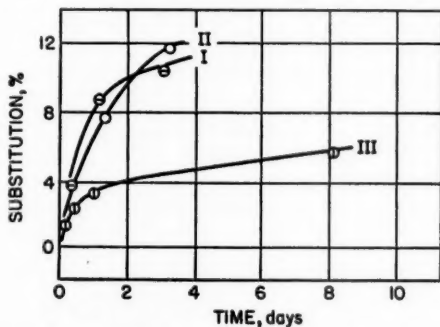


FIG. 6.—Rate of substitution of iodine monochloride in several polymers (temperature, 30° C; in the dark): I, natural rubber; II, sodium polyisoprene; III, GR-S.

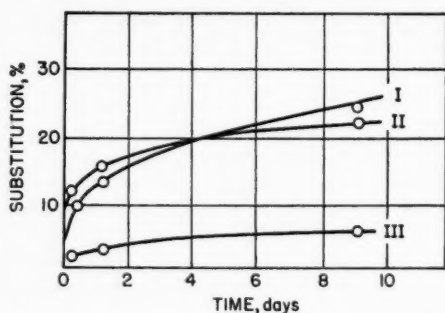


FIG. 7.—Rate of substitution of bromine in several compounds (temperature, 30° C; in the dark): I, oleic acid; II, undecylenic acid; III, styrene.

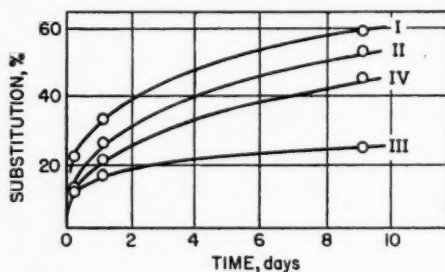


FIG. 8.—Rate of substitution of bromine in several polymers (temperature, 30° C; in the dark): I, natural rubber; II, sodium polyisoprene; III, GR-S; IV, polystyrene.

SUBSTITUTION REACTION

It has been mentioned above that the amount of substitution for various types of polymers is different. The amount of substitution in several simple, low molecular compounds over long periods of time is shown in Figure 5 (concentrations the same as those in Procedure I). The substitution of polymers during long reaction periods is shown in Figure 6. For comparison, the data for the substitution with bromine under the same conditions in the low molecular compounds and polymers are plotted in Figures 7 and 8. It is evident that the rate of substitution of bromine is five to ten times as large as the rate of substitution of iodine monochloride during the early stages of reaction. It has been observed that large amounts of acetic acid suppress substitution of iodine monochloride². However, the presence of acetic acid in the solvent decreases the solubility of the addition products of the polymers (see below) and should generally be avoided.

Under the conditions of Procedure I, iodine (0.01 *M*) was found to retard the substitution, but not to a large extent. Anhydrous hydrochloric acid (0.01 *M*), benzenesulfonic acid (saturated), and chloranil (0.01 *M*) were found to have no appreciable effect.

SOLVENT IN REACTION MIXTURE

The choice of solvent used in the determination of unsaturation must be based on two factors: (1) the solubility of the polymer-iodine monochloride addition product in the solvent and (2) the stability of the solution of iodine monochloride.

In general, the untreated polymers are more soluble in organic solvents than their addition products. The iodine monochloride addition product of polybutadiene is considerably less soluble than butadiene-styrene or polyisoprene addition products, and at 25° C the former precipitates immediately from carbon tetrachloride, chloroform, *o*-dichlorobenzene, or 50 chloroform-50 *p*-dichlorobenzene. Carbon disulfide is a better solvent for the polybutadiene addition product, and precipitation occurs only slowly at 25° C.

If precipitation occurs during the reaction of iodine monochloride with a polymer, low results for unsaturation are usually obtained. The precipitated product contains unreacted double bonds which react only very slowly on further standing. For example, emulsion polybutadiene, which was known to have an unsaturation of 97.7 per cent (Procedure I), was found to have an unsaturation of 91.5 per cent after one hour and 96.2 per cent after 19 hours at 25° C when 90 chloroform-10 carbon tetrachloride was employed as solvent.

Chloroform, carbon disulfide, carbon tetrachloride, and their mixtures in varying proportions were investigated systematically as solvents, and it was found that a 60-40 mixture of carbon disulfide and chloroform was the best solvent for the polybutadiene addition product. It was found, for example, that when solutions of iodine monochloride and polybutadiene were mixed under the conditions of Procedure I at 0° C, a turbidity appeared after 0.8 hour in a 70-30 mixture, 15 hours in a 60-40 or 50-50 mixture, and 0.7 hour in a 40-60 mixture. The precipitation from 50 carbon disulfide-40 chloroform-10 carbon tetrachloride was immediate at 0° C. (It is interesting to note that the 60 carbon disulfide-40 chloroform mixture dissolves polymers five to ten times as rapidly as either of the components does alone.)

It would be desirable to use carbon tetrachloride as a solvent for the stock solution of iodine monochloride, inasmuch as such a stock solution is somewhat more stable than one in chloroform. However, the presence of carbon tetrachloride decreases the solubility of the addition product considerably and is not recommended for analysis of polybutadiene. In the analysis of other types of polymers a 90 carbon disulfide-10 carbon tetrachloride mixture (stock solution 0.22 *M* iodine monochloride in carbon tetrachloride) can be used.

The two solvents recommended by Kemp and Peters, mixtures of *p*-dichlorobenzene, chloroform, and carbon tetrachloride, and of *p*-dichlorobenzene, carbon disulfide, and carbon tetrachloride, are poor solvents for the polybutadiene addition product. Other polymer addition products are, however, soluble in these mixtures. The solvents used by Kemp and Peters are especially adapted to the analysis of polymers containing gel or even of vulcanized polymers, inasmuch as the original sample can be heated with *p*-dichlorobenzene to 180° C to effect solution before the addition of the other reagents.

With regard to stability of iodine monochloride, carbon tetrachloride and carbon disulfide are the most suitable solvents. The decomposition of a 0.02 *M* iodine monochloride solution in 90 carbon disulfide-10 carbon tetrachloride was found to be only 0.5 per cent after 12 days in the dark at 25° C. However, on mixing carbon disulfide and iodine monochloride a slight reaction occurs, and the use of carbon disulfide as a solvent for the stock solution should therefore be avoided.

Iodine monochloride is also stable in pure, dry chloroform. On the other hand decomposition occurs at the rate of about 1.5 per cent per day at 25° C in the dark if the chloroform contains 0.8 per cent ethanol, the usual amount in commercial, reagent grade chloroform (present as inhibitor of decomposition).

If chloroform is to be used in the stock solution of iodine monochloride, the alcohol must be removed.

SUMMARY

The unsaturation of GR-S at various conversions corresponds to the spectrophotometrically determined styrene content. It is concluded that GR-S at various conversions has the theoretical unsaturation. Emulsion polybutadiene was found to have 97 to 98 per cent of the theoretical unsaturation, emulsion polyisoprene 97 per cent. Sodium polybutadiene and polyisoprene had unsaturations which were considerably less than theoretical. The unsaturation of sodium polybutadiene was 92 per cent and that of sodium polyisoprene was 85 per cent. Sodium copolymer of butadiene (75) and styrene (25) also had an unsaturation considerably less than the theoretical value.

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NATURAL VULCANIZATION ACCELERATORS IN HEVEA LATEX *

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As numerous investigators have shown, some of the nonrubber components of Hevea latex have a decided accelerating action on the process of vulcanization. A survey of the literature on this subject points to the validity of certain general facts.

1. Among the nonrubber components of latex which have been investigated, certain nitrogenous bases appear to be most important for accelerating the rate of vulcanization.

2. These nitrogen bases apparently occur partly naturally in fresh latex, and partly as the result of putrefaction, heating, and other decomposition processes.

3. The nitrogen bases naturally present in fresh latex at later stages have been identified by Altman¹ to be trigonelline, stachhydrine, betonicine, choline, methylamine, trimethylamine, and ammonia. These bases are markedly active in vulcanization, as will be seen in the section on experimental results.

4. The nitrogenous substances formed by the decomposition processes have only partly been identified, on the one hand as tetra- and pentamethylene diamine and some amino acids², on the other hand as alkaloids, proline, diamino acids, etc.³.

5. It has been generally accepted that these nitrogenous substances are derived from the proteins of the latex.

6. Decomposition appears to be connected with the formation of a considerable amount of acids⁴.

7. The production of volatile nitrogen bases as a rule accompanies the decomposition processes. These volatile products have not been identified.

8. The active nitrogen bases, either already formed or derived from complex nitrogenous substances, seem to be soluble in water but only slightly soluble in acetone.

These statements indicate that latex, in the fresh state, as well as after putrefaction, contains powerful natural accelerators. The active components in fresh latex may be identified as the organic bases mentioned above. The accelerators formed after putrefaction has taken place may be derived either from lecithins and cephalins or from proteins, which can form several bases on putrefying⁵.

Lecithins and cephalins form powerful accelerators on saponifying. The formation of strong acids, then, is quite comprehensible, since these complex fats contain phosphoric acid, which is easily separated by hydrolysis in the form of its glycerol ester⁶.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 40, No. 2, pages 241-249, February 1948. An extensive survey of the literature, with 84 references in addition to those appended to the present version, is omitted. The present address of the author is Laan van Meerdervoort 52H, The Hague, Holland.

The bases derived from putrefied proteins have not yet been separated or identified by the present author; there are, however, certain indications that these bases are also important as vulcanization accelerators, for example, in slab rubbers.

METHOD FOR TESTING ACCELERATING ACTION

It is certainly to be deplored that uniformity of testing methods and compounds is completely lacking. Some investigators used pure-gum mixes, others technical mixes with only zinc oxide or with zinc oxide and organic accelerators. The committee organized in 1935 by the Division of Rubber Chemistry of the American Chemical Society⁷ proposed the following compound, known as A.C.S. compound: 100 rubber, 3.5 sulfur, 6 zinc oxide, 0.5 stearic acid, and 0.5 mercaptobenzothiazole.

This mix was used in these tests, but the organic accelerator was replaced by the latex fractions. The fractions were used in higher concentrations than indicated by the A.C.S. compound; in general 2 grams and when possible even 5 grams of the fractions were mixed with 100 grams of rubber. In two cases—namely, in the tests of the water-solubles—acid lead acetate and of the ether-solubles—organic acids—the amount of zinc oxide was raised to 20 per cent to dull the strong acid character of these fractions. The A.C.S. mixes, containing either the prescribed proportion of mercaptobenzothiazole or no accelerator at all, served as controls.

As ordinary crepe and sheet always contain nonrubber components which possibly influence the rate of vulcanization, it was considered desirable to use purified rubber in the experiments. The crepe was derived from latex which was treated according to the method of Braak⁸; it had the following characteristics: ash 0.11 per cent, nitrogen 0.11 per cent, acetone extract 2.67 per cent, and copper 0.9 mg. per 100 grams of rubber.

It is known that the temperature and time of vulcanization are of great importance in the rate of cure. Concerning the influence of the vulcanization temperature, it can be assumed that a rise of 10° C accelerates the rate of cure two to three times.

In the experiments to be described three series of vulcanizates were made: (1) 127° C for 40 minutes, (2) at 127° C for 120 minutes, and (3) at 147° C for 75 minutes.

The characteristics of the vulcanizates, when not too soft for investigation, were estimated in the usual way. Thus, the tensile strength at break in kg. per sq. cm. (TSB), the tensile stress at 700 per cent elongation (TS 700), and the elongation at break (EB) in percentage were measured with the aid of the Schopper machine, whereas the hardness (H) was determined with the Shore durometer.

EXPERIMENTAL RESULTS

Activity of main fractions.—First of all the main fractions have to be investigated for their accelerating properties. The experimental data (Table I) show that the ether-solubles are most important for a further tracing of the active components. The water-solubles, although in far lower concentration, also contain substances with accelerating properties. However, the activity of the solids if present at all, is only slight, whereas the precipitate in a concentration of only 1.5 per cent shows no activity at all. These results show that natural accelerators are present in the latex-composing fractions which, therefore, have to be investigated more extensively.

TABLE I
ACCELERATING ACTION OF MAIN FRACTIONS

[illegible]

Activity of water-solubles.—The activity of the subfractions obtained from the water-solubles according to the method already described (Figure 3) is shown in Table II.

The figures obtained show that the water-soluble accelerators do not occur in the acid or in the ammoniacal lead acetate fraction. The filtrate, on the other hand, shows a much better accelerating activity than the main fraction. Consequently, the filtrate contains the natural accelerators in a higher concentration than do the total water-solubles. The results of experiments 10 and 11 lead to the conclusion that the amines are the main active components in this series. Amino acids had been repeatedly found inactive or only slightly active.

Activity of ether-solubles.—From the figures of Table I it appears that the ether-solubles contain a powerful accelerator (Experiment 4b). For this reason this fraction was separated, on the one hand, into acetone-solubles and acetone-insolubles, and on the other hand into unsaponifiables, organic acids, and second water layer.

The obtained results (Table III) point to the acetone-insolubles and to the second water layer as the most important subfractions of the ether-solubles. The other fractions, however, have little or no influence on the rate of cure.

As already mentioned, the acetone-insolubles contain principally lecithins and cephalins, whereas the second water layer is composed of the water-soluble saponification products of the fats and phospholipids—glycerol phosphoric acid, choline, etc. From these facts it seems obvious that the last-mentioned

TABLE II
ACCELERATING ACTION OF WATER-SOLUBLE SUBFRACTIONS

[illegible]

organic bases form the key to the solution of the problem of natural vulcanization accelerators. Consequently, choline phosphate (prepared from Kodak's choline hydrochloride) is tested for its accelerating properties with the striking result given in Table IV. (The activity of colamine, which was not available, was not investigated separately.) As choline base easily forms trimethyl-

TABLE III
ACCELERATING ACTION OF ETHER-SOLUBLE SUBFRACTIONS

Expt. No.	Accelerator (grams per 100 grams rubber)	Characteristics of vulcanizates obtained in series											
		a				b				c			
		TS 700	TSB	EB	H	TS 700	TSB	EB	H	TS 700	TSB	EB	H
1	None (control I)	—	—	—	—	—	—	—	—	—	1	399	17
2	Mercaptobenzothiazole (control II), 0.5	4	49	912	34	25	78	872	36	12	38	934	32
4a	Ether-solubles, total, 2	—	—	—	—	—	—	—	—	—	3	423	23
4b	Same, 5	—	—	—	—	—	—	—	—	7	51	1076	34
12a	Acetone-insolubles, 2	—	—	—	—	—	—	—	—	Damaged ^a	—	—	28
12b	Same, 4	—	—	—	—	3	4	940	20	12	72	963	25
13a	Acetone-solubles, 2	—	—	—	—	—	—	—	—	—	—	—	—
13b	Same, 5	—	—	—	—	—	—	—	—	—	5	435	20
14a/b	Unsaponifiables, 2, 5	—	—	—	—	—	—	—	—	—	—	—	—
15a/b	Organic acids, 2, 5	—	—	—	—	—	—	—	—	—	—	—	—
16a	Same, but with 20 parts ZnO, 2	—	—	—	—	—	—	—	—	—	1	299	16
16b	Same, 5	—	—	—	—	—	—	—	—	—	2	390	20
17	2nd water layer, 2	—	—	—	—	9	43	1059	30	20	81	899	36

^a The vulcanizate obtained, although having a good outward appearance, could not be tested on the Schopper machine, as air bubbles damaged the vulcanization plate at different places.

TABLE IV
ACCELERATING ACTION OF CHOLINE SALTS AND TRIMETHYLAMINE

Expt. No.	Accelerator (grams per 100 grams rubber)	Characteristics of vulcanizates obtained in series											
		a				b				c			
		TS 700	TSB	EB	H	TS 700	TSB	EB	H	TS 700	TSB	EB	H
1	None (control I)	—	—	—	—	—	—	—	—	—	1	399	17
2	Mercaptobenzothiazole (control II), 0.5	14	49	912	34	25	78	872	36	12	38	934	32
18	Choline phosphate, 2	49	128	840	40	135	155	740	47	42	93	803	40
19	Trimethylamine phosphate, 2	—	—	—	—	6	8	764	25	13	37	860	32

TABLE V
ACCELERATING ACTION OF CHOLINE SALTS IN COMPARISON WITH MERCAPTOBENZOTHIAZOLE

Expt. No.	Accelerator (grams used per 100 grams rubber)	Characteristics of vulcanizates obtained after heating at 127° C for															
		20 min.				40 min.				60 min.				80 min.			
		TS 700	TSB	EB	H	TS 700	TSB	EB	H	TS 700	TSB	EB	H	TS 700	TSB	EB	H
20	None (control I)	2	2	906	20	2	2	1020	22	2	2	873	18	2	2	820	20
21	Mercaptobenzothiazole (control II), 0.5	16	37	826	30	34	88	852	38	50	109	829	40	56	116	820	41
22	Choline phosphate, 0.5	2	3	700	25	5	24	1062	28	12	53	975	30	15	90	1036	32
23	Choline carbonate, 0.5	5	21	1091	27	11	40	998	30	18	80	986	32	23	109	992	34

amine⁹, the latter compound was also tested in this series of experiments. The figures obtained show, however, that choline and not trimethylamine is the most active base.

A supplementary experiment was made to compare the accelerating activity of choline, in the form of its phosphate and its carbonate, with that of an equal quantity of mercaptobenzothiazole. The results obtained are given in Table V;

it can be safely concluded that choline base and mercaptobenzothiazole are equally good accelerators. Choline phosphate and choline carbonate contain only 60.2 and 85.0 per cent of choline base, respectively (Figure 5).

DISCUSSION

It seems clear that the active nitrogen-bases naturally present in fresh latex are identical with the amines and betaines separated earlier by the present author¹, and the active components formed after decomposition processes have taken place in the latex may be partly identified as the bases choline and colamine, present in latex in considerable quantities.

The active bases formed from putrefied or hydrolized proteins naturally present in latex have not yet been isolated or identified. Bruni and Levy² and Park, Carson, and Sebrell³ isolated certain active components from putrefied (matured) or heated latex; but there is no evidence that these compounds are derived from the proteins. Van Dalfsen¹⁰ stated that the vulcanizates of matured rubber attain an optimal tensile strength after 10-14 days' storage of the raw rubber. Some days later a lower tensile strength is found, which finally shows a second increase. The latter increase, however, is small and not convincing. In one case, when the rubber was coagulated with alum, the tensile strength after 60 days of maturation was found to have increased markedly.

In the light of the present author's findings, it seems clear that the large increase in tensile strength in the beginning of maturation must be due to the formation of choline and colamine from the lecithins and cephalins. The moment at which the optimal tensile strength is reached probably corresponds precisely with the moment at which the quantities of the mentioned bases (in grams) reach their maximum. The decrease in tensile strength observed afterwards may be considered a consequence of the decomposition of choline into trimethylamine, which was shown (Experiment 19) to be far less active than choline. Moreover, as trimethylamine is a volatile compound, it can easily escape into the air.

The incidental increase in tensile strength after 60 days' storage is remarkable. According to van Dalfsen this second rise in the tensile strength "must be ascribed to the action of accelerators from protein decomposition; indeed this increase coincides with considerable losses in the nitrogen content of the rubber". No attempt was made, however, to prove that the accelerating components are really derived from the latex proteins.

At any rate, of all the nonrubber components more or less active in the process of vulcanization, choline and colamine appear to be most important. It is, therefore, of interest to find out in which concentration these compounds occur in the latex. On the average, 1 liter of latex contains about 10 grams of ether-solubles, which are composed of approximately 45 per cent fats (acetone solubles), 33 per cent lecithins (insoluble in acetone but soluble in absolute alcohol), and 22 per cent cephalins (acetone and alcohol insoluble)¹¹. Consequently, 1 liter of latex contains about 0.5 gram of choline and 0.2 gram of colamine. Expressed in percentages of dry rubber, these figures amount to about 0.15 choline and 0.05 colamine. As is clearly demonstrated by Figure 1, which shows that only 0.3 gram of choline base on 100 grams of rubber power-

fully accelerates the rate of cure, the naturally occurring quantities are sufficient for causing a perceptible acceleration of the vulcanization process.

It was shown by the present author¹ that the quantities of nitrogen bases naturally present in fresh latex amount to 0.1 per cent of the latex when expressed as hydrochlorides. At present the influence of this small quantity on the rate of cure is unknown.

No exact quantitative data are available concerning the prolamines occurring in latex¹².

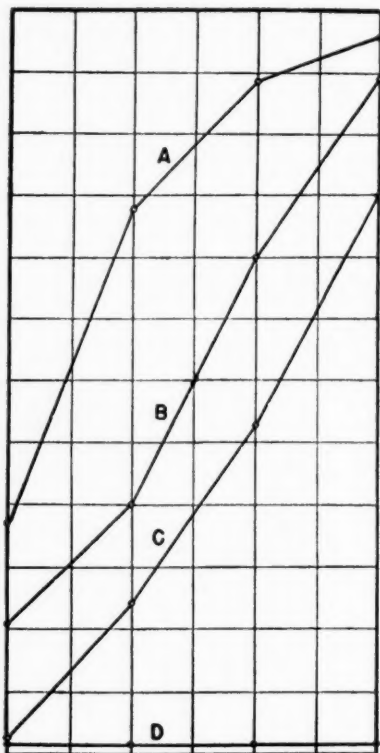


FIG. 1.—Effect of various accelerators on rate of cure.
A, mercaptobenzothiazole; B, choline carbonate; C, choline phosphate; D, no accelerator.

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EFFECT OF PROLONGED STORAGE OF UNVULCANIZED STOCK ON THE PROPERTIES OF THE VULCANIZATE *

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INTRODUCTION

The object of the experiments was to determine how the properties of a vulcanized natural rubber tread stock (as used for retreading) are affected by previous storage of the unvulcanized stock for long periods. A parallel series of tests was made in which the vulcanized stock was similarly stored, in which case the observed aging changes were compared with those resulting from aging of the unvulcanized stock.

EXPERIMENTAL

Four stocks, designated A, B, C, and D, were made up by different manufacturers from the same formula: smoked sheet rubber 100, sulfur 2.9, MPC black 49, zinc oxide 7.9, Paraflux 1.15, pine tar 1.6, stearic acid 2.85, mercaptobenzothiazole 0.8, phenyl-beta-naphthylamine 1.3; a fifth stock (mixed stock) was made by blending equal parts of A, B, C, and D.

Sheets about 0.1 in. thick of each stock, for tensile and hardness tests, were vulcanized for 10, 30 (optimum), and 180 minutes at 145° C; abrasion (Akron) and flexing (De Mattia) specimens were vulcanized for the 30- and 180-minute periods, plus a 5-minute rise on account of the thicker molds.

Both vulcanizates and unvulcanized stocks were stored in the dark at a temperature normally between about 10° and 15° C and never exceeding 25° C, tests being made after the following periods:

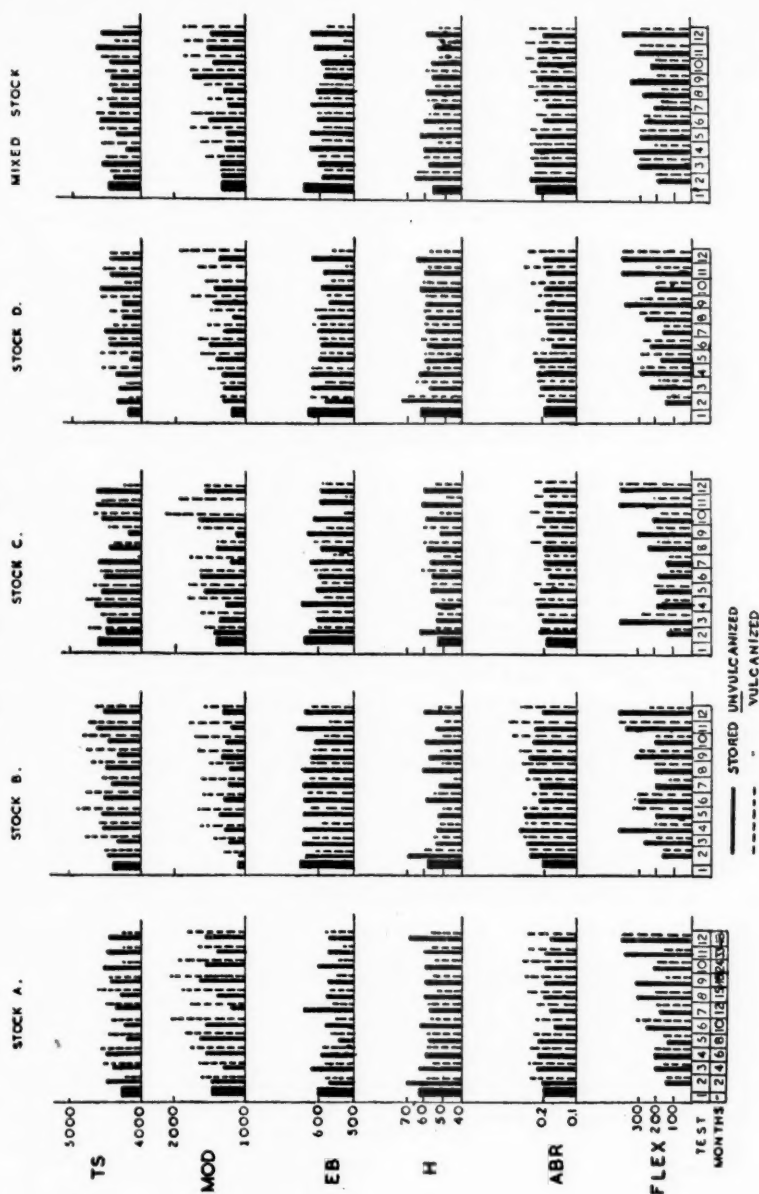
Test No.:	1	2	3	4	5	6	7	8	9	10	11	12
Storage (months):	0	2	4	6	8	10	12	15	18	24	33	48

The unvulcanized stocks were in the form of extruded tread sections, approximately 6 in. \times $\frac{1}{2}$ inches, rolled up between glazed holland cloth; after each storage interval the portions of stocks A-D required for vulcanization were remilled and sheeted to a convenient thickness for molding, and the mixed stock was made by blending stocks A-D. Milling conditions were standardized as follows: roll temperature, 52° C, at start, cooling to 43° C (mean roll temperature varying not more than $\pm 3^\circ$ C in different tests); milling time, 17 ± 5 minutes. These portions, after resting for 1-2 days, were vulcanized as described above.

Test methods were as follows: *Tensile tests*: as B.S. 903-1940, using type B dumbbells; *Hardness*: R.A.B.R.M. gauge, with $\frac{1}{4}$ -inch ball and 1000-gram load on 5 mm. thickness of rubber (this investigation was started before the method of B.S. 903 had become established, but the hardness numbers quoted are ap-

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PHYSICAL TESTS ON VULCANIZED TIRE-TREAD STOCKS AFTER PROLONGED
STORAGE IN THE UNVULCANIZED AND VULCANIZED CONDITIONS.
VULCANIZATION 30 MINS. AT 145°C.



proximately equal to B.S. Hardness Numbers); *Abrasion*: Akron machine, using the conditions described in "Rubber: Physical and Chemical Properties," p. 540; *Flexing*: De Mattia machine, test conditions as in A.S.T.M. Designation D430-40, Method B, Bend Flexing.

Results for the 30-minute (optimum) vulcanizates are given in the figure, in which the properties are denoted as TS (tensile strength, lb. per sq. in.),

MOD (modulus, lb. per sq. in., at 300 per cent elongation), EB (percentage elongation at break), H (hardness number, as indentation in mm./100, ABR (abrasion loss, cc. per 1000 revolutions of the abrasive wheel), FLEX (kilocycles of flexing required to produce cracking to Grade 3 on an arbitrary scale from 0, uncracked, to 10, completely broken).

As the results for the 10-minute and 180-minute vulcanizates indicated substantially the same conclusions as the 30-minute vulcanizates, they are not reproduced in this report.

DISCUSSION

It is at once obvious from the graphs in the figure that storage of the unvulcanized stocks for a period of four years has not led to any serious deterioration in the properties of the optimum vulcanizate. In no case is there any significant loss of tensile strength or of resistance to abrasion or flex-cracking. There even appears to be a tendency for flex-cracking resistance to improve but, in view of the magnitude of the experimental error, this cannot with certainty be claimed as a real effect. Breaking elongation is usually slightly lowered by prolonged storage of the stock, but even after four years this change amounts only to some 20-40 per cent elongation. In keeping with this there is in some cases a tendency for the modulus to become greater and the vulcanizate harder, but again neither of these effects is of any practical consequence.

A study of the results for the 10-minute and 180-minute vulcanizates made from stock stored for various periods shows no substantial difference from the behavior just described for the 30-minute vulcanizates, except that with the 10-minute vulcanizates the loss of elongation after four years is perhaps greater, namely, 30-70 per cent elongation. In particular, no tendency was observed for the modulus or hardness of the 10-minute vulcanizate (which represents a very pronounced undercure) to change as a result of prolonged storage of the stock. This shows that such storage did not appreciably affect the rate of vulcanization.

In contrast to the above results of storage in the unvulcanized condition, storage of the vulcanizates caused decidedly more pronounced stiffening (increase in modulus), hardening, and loss of elongation, as can be seen from the graphs in the figure. These differences were noticeable at all the three states of vulcanization examined. As might be expected from these changes in modulus, hardness, and elongation, the resistance to flex-cracking is definitely poorer in the samples stored in the vulcanized condition, and this is true also of abrasion resistance. On the other hand, tensile strength tends on the average to be rather higher in these samples than in those prepared from material stored as unvulcanized stock.

The changes observed to result from storage of the vulcanizates are just those that would be expected to occur during natural aging. Even the tendency for the tensile strength to rise, at least during the early stages, is not unexpected in a rubber possessing good resistance to aging.

SUMMARY

The effects of prolonged storage, in both the unvulcanized and vulcanized states, on the physical properties of four samples of tire tread stock were studied. Storage of unvulcanized stock for four years did not cause any appreciable change in its rate of vulcanization or in the deterioration of any of the important

properties of the vulcanizate. Comparison with the results for samples stored in the vulcanized condition shows that the unvulcanized stock was, in fact, more stable than the vulcanizate as far as changes during storage were concerned.

ACKNOWLEDGMENT

This investigation, commenced in 1939, was undertaken on behalf of Tyresoles, Ltd., to whom the Association is indebted for permission to communicate the results.

EFFECT OF STORAGE AND TEMPERATURE ON FLEXIBILITY OF NATURAL AND SYNTHETIC RUBBERS *

JOHN B. GREGORY, IRVING POCKEL, AND JOHN F. STIFF

CHEMICAL WARFARE SERVICE

Prior to World War II little thought had been given to possible failure of gas mask faceblanks and hose tubes at low temperatures as natural rubber was used, and no trouble with stiffening of the natural rubber masks due to low temperature use or storage had been reported. With the replacement of natural rubber by GR-M (Neoprene) in 1943, it was recognized that the low temperature flexibility of this material might be a problem. An extensive investigation of the best formulations for cold resistance was therefore made, and the specifications were written so that formulae with the best low temperature properties would be used. Although GR-S (butadiene-styrene copolymer) and GR-M were both available for gas masks at that time, GR-M was selected since no method was then known for satisfactorily compounding GR-S to give the necessary physical characteristics at normal temperatures. However, in spite of all efforts to produce the best GR-M compound possible, a variety of complaints was received from the European Theater of Operations because of stiffening of the GR-M masks on long-time storage at the rather low temperatures encountered.

Gas masks may often be exposed to low temperatures for long periods before wearing if required for use in cold weather. Few investigators until recently¹, however, have used sufficiently long exposure times in their test methods to study the effect of such long exposure. In the evaluation of compounds for rubber gas mask facepieces where the requirement is that the flexibility must remain relatively constant as the temperature changes in order that a proper fit may be obtained, the measurement of brittle point or T-50 value is not applicable². Even the determination of modulus at 200% elongation at different temperatures is not suitable, as gas masks are so constructed that elongations of even 5% are seldom required. Moduli at lower elongations than 200% are not easily measured with standard equipment.

As Liska³ has already given a good review of early work on the effect of low temperatures on elastomers, a detailed account will not be repeated here. We would, however, like to emphasize that care must be used in predicting performance of rubber stocks from brittle point data alone. For example, from the results of brittle point tests, Selker, Winspear and Kemp⁴ state that natural rubber compounds containing no sulfur have a lower brittle point than compounds that have been vulcanized with sulfur and that the brittle point tends to rise with increases in combined sulfur content. Gibbons, Gerke and Tingey⁵ have shown by use of the T-50 test, however, that the re-

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sistance of rubber compounds to freezing increased with increases in per cent combined sulfur and in length of cure.

It seems to us that the occurrence of the two distinct changes when an elastomer such as natural rubber is cooled: namely true crystallization and second-order transition, explains anomalies such as the above. Liska³ discusses these changes and states that they were demonstrated by investigators at the National Bureau of Standards. It might well be that owing to the rapid lowering of the temperature in the brittle point test⁴ the internal viscosity of the rubber increases so rapidly that crystallization is inhibited and second-order changes predominate. The results obtained by the T-50 test⁵, on the other hand, probably are more affected by the crystallization tendency. Sulfur vulcanization with its inhibiting effect on crystallization by cross-linking and its general stiffening of the system might well be expected to give the apparently contradictory results reported.

In order to study the properties of gas mask rubber, the CWS flexibility test for coated fabrics developed by O. Morningstar and I. Pockel at the CWS development laboratory was adapted to elastomer testing.

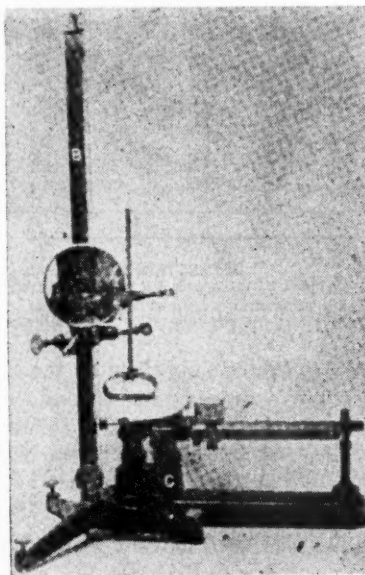


FIG. 1.—Device for determining flexibility of elastomers—(A) ring loop; (B) cathetometer; (C) balance.

DIRECTIONS FOR THE OPERATION OF THE TEST

The test, apparatus for which is shown in Figure 1, consists essentially in loading and unloading a loop-shaped rubber sample in successive increments and measuring each resulting deformation of the sample. The sample, a one- by six-inch piece cut from an A.S.T.M. test slab⁶ is bent and held in a clamp which in turn is attached to the movable element of a cathetometer⁷. The apparatus is assembled so that the platform of a triple beam balance at zero load just touches the under side of the loop.

When the sliding weight on the balance arm is moved to a new position, not zero, the platform moves vertically upward and deforms the loop. By appropriately turning the cathetometer dial, the loop is compressed until the balance index again indicates level. Hence the stresses in the rubber sample are just sufficient to equal the external load shown on the balance arm. Figure 1 illustrates the apparatus with a ring under a slight load. The load is added in increments of about one-tenth the total necessary to collapse the loop almost completely. A balance is obtained, by means of the cathetometer, after each additional loading interval. The ring is then unloaded in successive increments balancing after each unloading.

To allow time for the slight creep or flow of the rubber, a one-half minute interval is allowed to elapse between each change in load and the corresponding reading of the cathetometer. The cathetometer is turned during this time interval so as to maintain instrument balance.

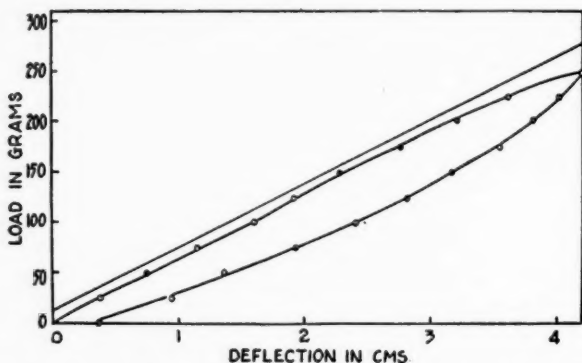


FIG. 2.—Load vs. deflection for a loop of natural rubber—tan alpha = 66; average thickness = 0.064-inch; $S = 209$; resilience = 74%.

Figure 2 shows some typical data obtained by the above method plotted on rectangular coordinate paper. The average slope of the curve obtained in this way, which is a measure of the stiffness, is empirically designated as tangent alpha. The ratio of the areas under the loading and unloading curves determined by a planimeter multiplied by 100 give the per cent resilience of the sample.

DETERMINATION OF FACTOR FOR CONVERTING TAN ALPHA TO "S"

In order to determine a coefficient of flexibility of elastomers independent of the thickness of the sample a formula was devised for converting tan alpha to "S", where "S" is the coefficient of flexibility. Slabs of various thickness from representative Neoprene and GR-S stocks were molded, and values of tangent alpha determined on specimens cut from these slabs and plotted on logarithmic paper against the thickness of the samples. Straight lines were obtained with a slope of 2.5 indicating that tangent alpha varied inversely with the 2.5 power of the thickness. Tangent alpha was therefore converted to S according to the following equation— $S = \frac{10^5 \text{ Tan } \alpha}{T^{2.5}}$, where S is the coefficient of flexibility characteristic of the material and T is the thickness in thousandths of an inch.

EFFECT OF USING SHORT SAMPLES ON "S"

The effect on the "S" value of using strips shorter than six inches was determined on samples of various lengths cut from miscellaneous GR-M samples of varying flexibility. From these data a graph was obtained so that a true "S" could be attained on such samples (see Figure 3).

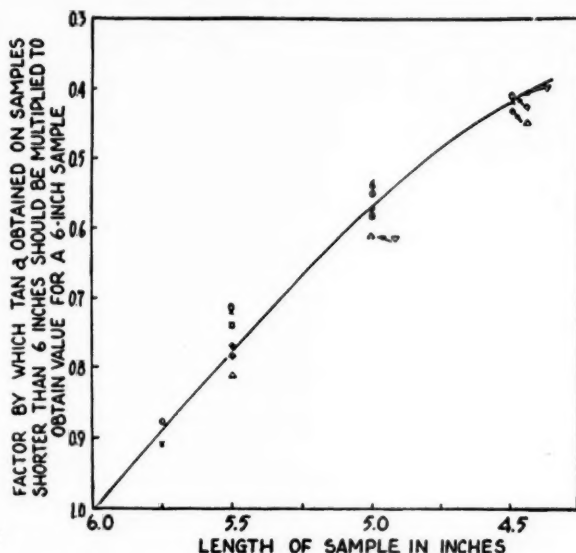


Fig. 3.—Corrections to be applied to tan alpha obtained on samples shorter than six inches.

EXPERIMENTAL DETAILS

The coefficient of flexibility or the per cent resilience of elastomers can be determined by this method at various temperatures by placing the sample to be tested and the test apparatus in a thermostatically controlled cold or hot room. The machine is somewhat bulky, and considerable manipulation of the sample is involved so that its use in small ovens or cold boxes is not recommended.

With the use of the above test method a study was made of the behavior of various gas mask faceblank compounds after prolonged storage at various temperatures.

Detailed formulations and physical properties of the rubber gas mask faceblank stocks selected are shown in Table 1. The stocks were compounded and A.S.T.M. slabs⁶ molded using standard rubber laboratory equipment and technique.

Two one-by-six-inch strips of each stock were stored at -20 , $+5$, $+35$, and $+150^{\circ}\text{F}$ and their respective flexibilities determined periodically at the storage temperatures, except in the case of those strips stored at 150°F ; the latter were conditioned at 70°F for 24 hours before testing, and then tested at 70°F .

Figure 4, showing the plots of "S" value vs. time in storage at 150°F for each stock, shows that all stocks increase in stiffness somewhat during the first two weeks of storage. The reclaim stock No. 5 is the worst, and the natural rubber stock No. 7 the best. As an "S" value of 70 was found to be about the

TABLE 1
 FORMULAS OF STOCKS USED IN STUDY OF EFFECT OF LONG-TIME
 EXPOSURE AT VARIOUS TEMPERATURES ON FLEXIBILITY

Compound No.	1	2	3	4	5	6	7
GR-I	100						
GR-S		100					
GR-M			100	100			
Smoked sheet					61	100	100
Midwest reclaim 13A					90		
Stearic acid	1.5		1	1	1.68	2	2
Zinc oxide	5	5	12	12	18.6	5	5
Sym. di-beta-naphthyl-para-phenylenediamine					1.18	1	1
Flectol H					.77		
Salicylic acid					.13		
Mercaptobenzothiazole					1.86		
N-cyclohexyl-2-benzothiazole sulfenamide					.17		
Di-ortho-tolylguanidine salt of dicatechol borate			0.35	0.35			
Sodium acetate			0.5	0.5			
Methylene-paratoluidine		0.5					
Di-ortho-tolylguanidine		0.2					
Zenite		0.8					
Zenite A						1	1
Dimethylthiuram disulfide	1						
Selenium dithiocarbamate	1						
Red lead	0.5						
Extra-light magnesium oxide			1	1			
MPC black		20			4.34		
Calcene					107.5	142	25
FT black			15	15			
SRF black	70	16	30	30			
Phenyl-alpha-naphthylamine			4	4			
Heliozone		2			0.53		
Paraffin	4		2	2	1.53		
Petrolatum			1	1			
Dioctyl phthalate	12.5					1	1
Dibutyl sebacate	6.25						
Dicapryl phthalate			15	15			
Bayol D	6.25						
Light Circo Oil			5	5	10.4		
Mineral rubber		7.5					
Neophax A			10	10			
Naftolen R-100		6					
Sulfur	1.5	1.5		1	2.3	2	2
Cure	30	10	10	10	8	8	8
	Min. at 320° F	Min. at 320° F	Min. at 320° F	Min. at 320° F	Min. at 290° F	Min. at 290° F	Min. at 290° F
Physical properties							
Tensile p.s.i.	1553	1179	1924	1945	1415	2127	2937
Elongation (%)	723	878	802	770	540	686	718
Modulus at 200% p.s.i.	237	101	260	326	363	293	116
400% p.s.i.	465	286	881	966	891	866	426

upper limit for comfort, it is evident that the reclaim and 65% natural rubber are somewhat too stiff after storage. The GR-I compound also appears to be borderline.

The next figure, No. 5, shows, the effect of various low temperatures on the GR-I stock. No difference in the flexibility of the stock could be detected

initially or on long exposure at 70, 35, and 5° F or initially at -20° F. During prolonged exposure at -20° F a progressive change is, however, very marked. This is thought to indicate crystallization of the GR-I.

Figure 6, giving the plots for the GR-S stock at the same temperatures, shows no progressive decrease in flexibility with time of storage at any one temperature, but a decrease in flexibility at each lower temperature is quite

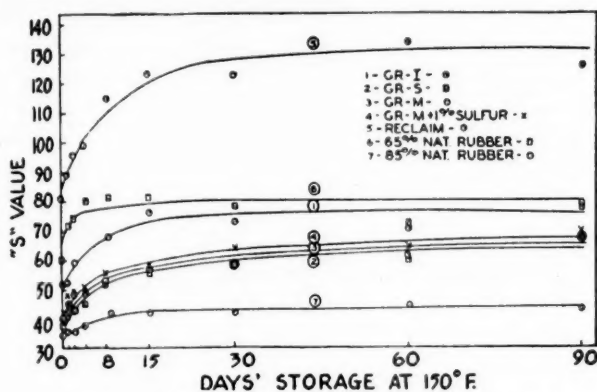


Fig. 4.—Flexibility of faceblank stocks from Table 1 at 70° F after storage at 150° F for various times.

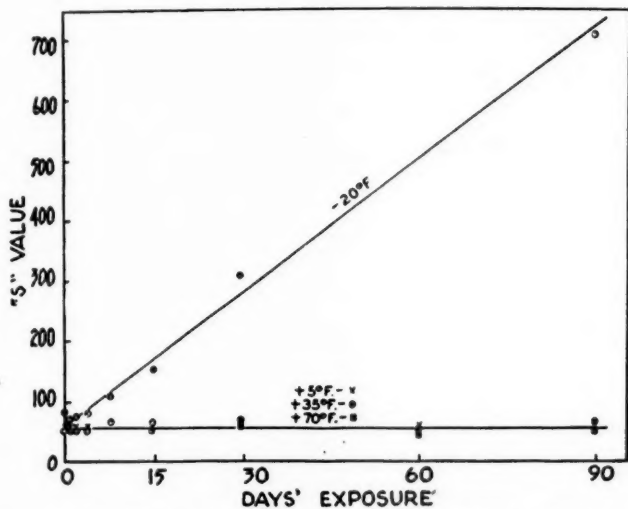


Fig. 5.—Stiffening of GR-I faceblank stock No. 1, Table 1, vs. days' exposure at various temperatures.

evident. Such changes, considered due to the effect of second-order transition, were not noted in the GR-I stock.

The plots for the GR-M stock at various low temperatures (Figure 7) show the effect of both crystallization and second-order transition. An interesting point about these curves is that they show that GR-M is more flexible at -20° F than at +5° F between two and 30 days' storage. It is felt that

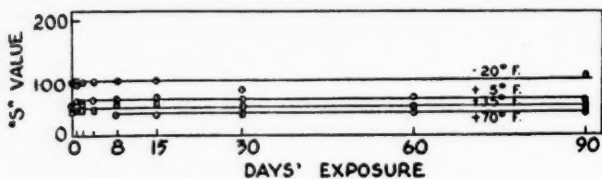


Fig. 6.—Stiffening of GR-S faceblank stock No. 2, Table 1, vs. days' exposure at various temperatures.

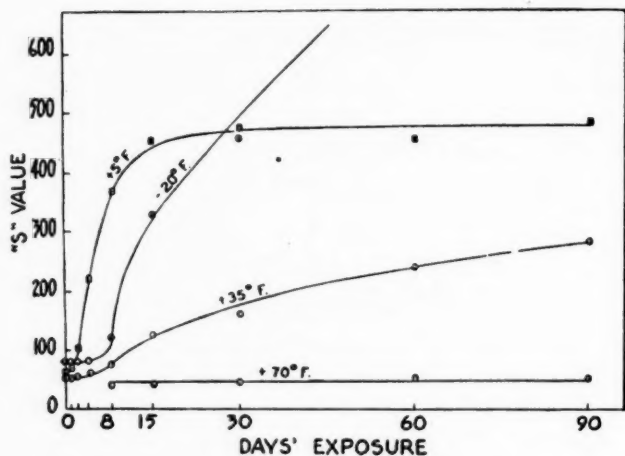


Fig. 7.—Stiffening of GR-M faceblank stock No. 3, Table 1, vs. days' exposure at various temperatures.

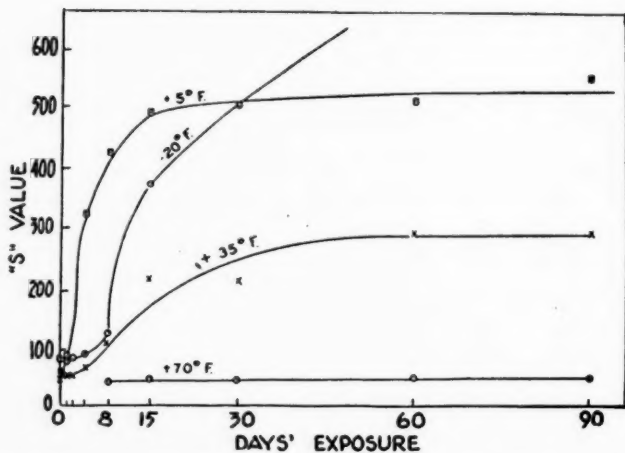


Fig. 8.—Stiffening of GR-MI+1% S faceblank stock No. 4, Table 1, vs. days' exposure at various temperatures.

this phenomenon is due to differences in the rate of crystallization of the polymer which apparently is near a maximum at $+5^{\circ}\text{F}$.

Figure 8 indicates that the addition of sulfur to the GR-M stock has little effect on its low temperature properties.

Reclaim rubber stocks too show both crystallization and changes due to second-order transition (see Figure 9). Figure 10 shows, however, that the

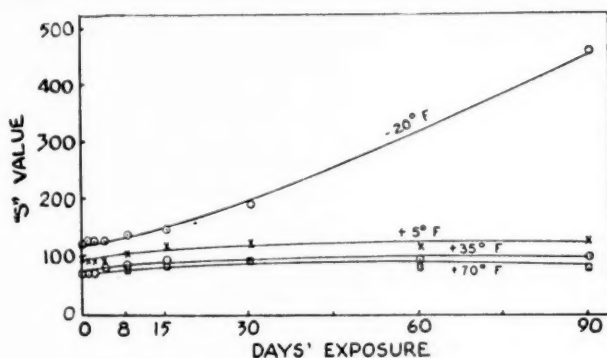


FIG. 9.—Stiffening of reclaim faceblank stock No. 5, Table 1, vs. days' exposure at various temperatures.

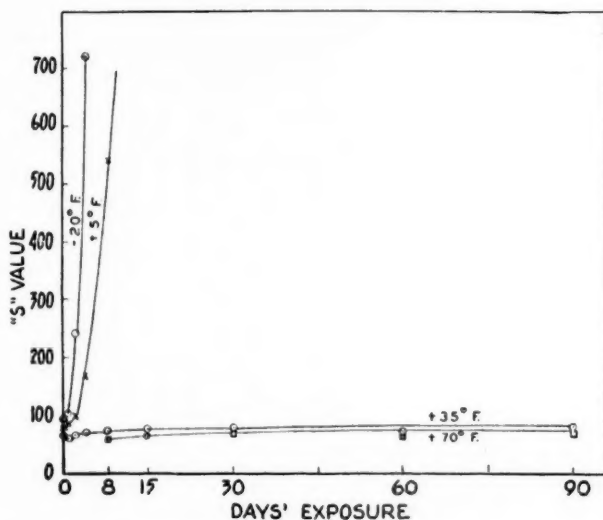


FIG. 11.—Stiffening of natural rubber faceblank stock No. 6, Table 1, vs. days' exposure at various temperatures.

100% smoked sheet compound has a much more pronounced tendency to crystallize at $+5$ and -20°F even though it also is heavily loaded. A pure gum stock with little filler shows the same crystallization tendency as the loaded stock (see Figure 11), but here no effect of second-order transition is noted. To avoid discomfort in the faceblanks due to high modulus, both these natural rubber stocks were compounded with but 2% sulfur. Natural rubber vul-

TABLE 2
 FORMULAS OF STOCKS USED IN STUDY OF EFFECT OF SULFUR CONTENT AND STATE OF CURE ON
 LOW TEMPERATURE FLEXIBILITY OF GR-I, GR-M, AND NATURAL RUBBER COMPOUNDS

Compound No.	8	9	10	11	12	13	14	15	16	17
GR-I	100	100	100	100	100	100	100	100	100	100
GR-M	5	5	5	5	12	12	12	30	100	100
Smoked sheets					1	1	1		30	30
Zinc oxide					1	1	1			
Extra-light magnesium oxide					1	1	1			
Red lead oxide	0.5	0.5	0.5	0.5	1	1	1	1.1	1.1	1.1
Stearic acid	1.5	1.5	1.5	1.5	0.5	0.5	0.5	0.15	0.15	0.15
Sodium acetate					0.5	0.5	0.5	1.1	1.1	1.1
Salicylic acid										
Sym. di-beta-naphthyl-para-phenylenediamine					4	4	4			
Phenyl alpha naphthyl amine					0.35	0.35	0.35			
Di-ortho-tolylguanidine salt of dicatechol borate										
Dimethyl thiuram disulfide	1	1	1	1						
Selenium dithiocarbamate	1	1	1	1						
Mercaptobenzothiazole								0.7	0.7	0.7
Santocure								0.24	0.24	0.24
Benzothiazyl disulfide					1	1	1			
S. R. F. black	70	70	70	70	30	30	30			
F. T. black					15	15	15			
Calcene					10	10	10	86	86	86
Factice	4	4	4	4	2	2	2		1	1
Paraffin										
Heliozone										
Petrolatum					1	1	1			
Dicapryl phthalate	6.67	6.67	6.67	6.67	15	15	15			
Dibutyl sebacate	6.67	6.67	6.67	6.67						
Diocetyl phthalate	6.67	6.67	6.67	6.67						
Light Circo Oil					5	5	5			
Sulfur	1.5	2	2.25	2.5	1	2	3	2	2.25	2.5
Cure:										
Min. at 320° F	30	30	30	30	30	30	30	8	8	8
Physical properties:										
Tensile p.s.i.	1457	1499	1275	1076	1867	1922	1982	2589	2561	2627
Elongation (%)	670	683	587	577	743	757	770	650	653	663
200% modulus p.s.i.	282	259	328	284	277	302	321	314	319	311
200% modulus p.s.i. (corrected)	142	150	142	126	232	250	265	338	298	218

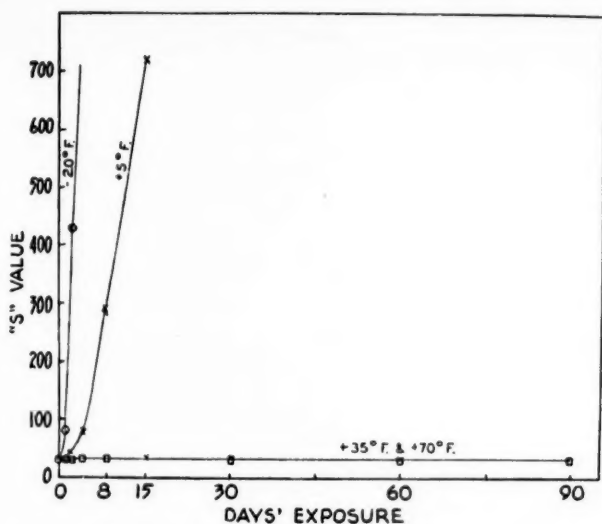


FIG. 10.—Stiffening of, natural rubber faceblank stock No. 7, Table 1, vs. days' exposure at various temperatures.

canized with more sulfur would have been more resistant to crystallization. To study the effect of per cent sulfur and time of cure on the low temperature flexibility of GR-I, GR-M, and natural rubber, the compounds shown in Table 2 were made up and A.S.T.M. test slabs⁹ molded using an undercure, optimum cure, and overcure. Strips of the GR-I and natural rubber compounds were then stored at -20°F and the GR-M strips at $+5^{\circ}\text{F}$. The flexibilities of these materials were determined periodically, and "S" values calculated.

Figure 12, showing the results with the GR-I compound containing 2% sulfur, indicates the importance of cure time. But varying the sulfur content from 1.5 to 2.5%, as shown in Figure 13, does not appear to be critical.

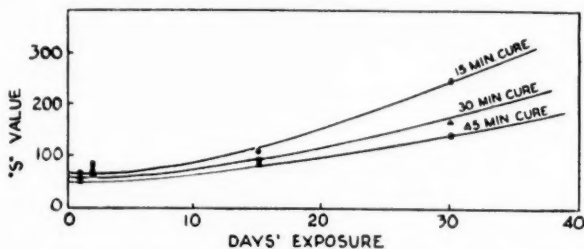


FIG. 12.—Effect of cure on flexibility of GR-I compound No. 9, Table 2, stored at -20°F .

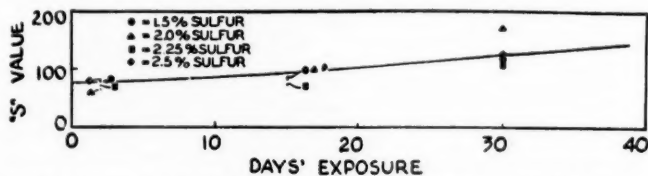


FIG. 13.—Effect of per cent sulfur on flexibility of GR-I compounds 8, 9, 10, and 11 on Table 2, stored at -20°F .

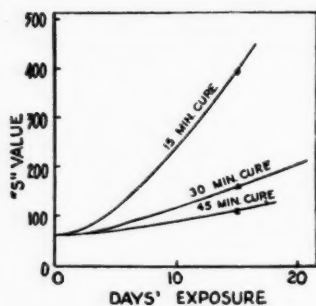


FIG. 14.—Effect of cure on flexibility of GR-M compound No. 14, Table 2, stored at -20° F.

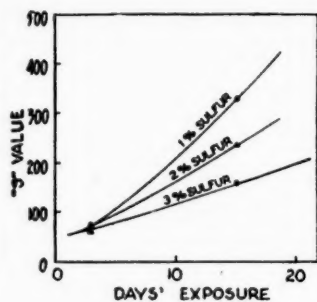


FIG. 15.—Effect of per cent sulfur on the flexibility of GR-M compounds 12, 13, and 14, Table 2, stored at -20° F.

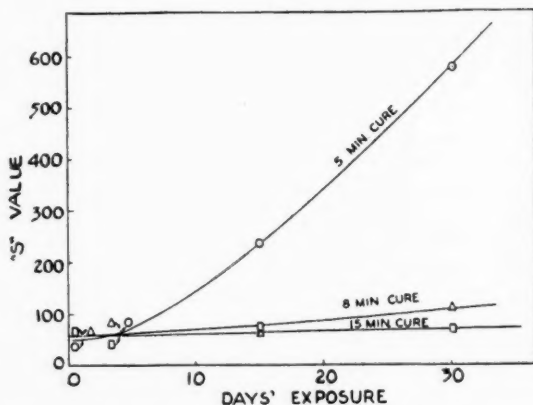


FIG. 16.—Effect of cure on flexibility of natural rubber compound No. 16, Table 2, stored at -20° F.

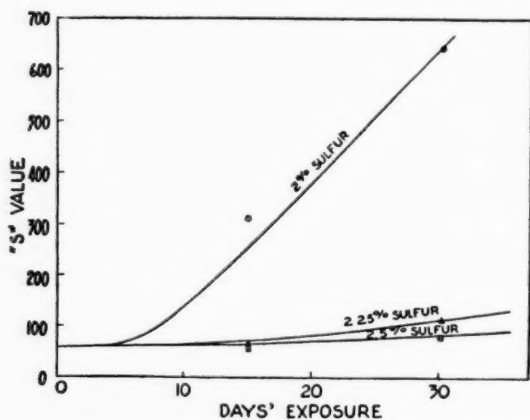


FIG. 17.—Effect of per cent sulfur on the flexibility of natural rubber compounds 15, 16, and 17, Table 2, stored at -20° F.

Figure 14 shows the effect of cure time on a GR-M compound containing 3% sulfur. Long cure times with stocks containing 3% sulfur resulted in virtual elimination of the stiffening effect in GR-M, but such stocks have undesirable modulus and inferior aging qualities. Figure 15 shows the effect of varying sulfur from 1% to 3%.

Figures 16 and 17 show the effect of cure on the natural rubber compound containing 2.25% sulfur and the effect of varying the sulfur in compounds No. 15, No. 16, and No. 17. Both cure and sulfur content are shown to be critical factors.

To determine the practical effect of the observed changes after storage at low temperatures in the flexibility of the gas mask faceblank stocks given in Table 1, faceblanks were molded and stored at $-5^{\circ}\text{F} \pm 5^{\circ}\text{F}$ for 30 days. Twelve natural rubber faceblanks of unknown composition were also stored with the above. The GR-M faceblanks, the natural rubber faceblanks made from compound No. 6 (Table 1), and most of the commercial natural rubber masks were found to be too stiff for use after this treatment; whereas the others were still usable. Twenty-four other commercial natural rubber masks were stored at $+5^{\circ}\text{F}$ for 60 days. At the end of this period two of the masks were too stiff for use; whereas the others were very flexible.

DISCUSSION

Using as a criterion that the stock shall not stiffen on prolonged exposure at low temperatures, it is apparent that if gas mask faceblanks were made from compounds given in Table 1 (see also Figures 7 to 14), only those made of the GR-S stock would be satisfactory. Conversely, this would indicate that faceblanks made of GR-I and natural rubber could not be used at temperatures at or below -20°F and $+5^{\circ}\text{F}$ respectively.

However, since no trouble with natural rubber faceblanks at low temperature has been reported even though they have been rather extensively tested under mild arctic conditions, it follows that GR-I as well as the GR-S should be a suitable synthetic for use in gas mask faceblank manufacture. Considerable improvement in the low temperature characteristics of GR-I compounds would nevertheless be highly desirable. Owing to the poor hot tear and hence poor molding characteristics of GR-I, the latter is considered the most satisfactory synthetic elastomer available for faceblank manufacture at present.

In addition to its tendency to stiffen at low temperatures, GR-M has another drawback when used for gas mask compounds. GR-M gas mask facepieces which have become stiff from exposure to the cold are difficult to render flexible again unless dipped into warm water (100°F) or hung in a warm room (80°F). Cold stiffened natural rubber or GR-I facepieces, on the other hand, are easily rendered flexible by the warmth of the body.

From the above work it appears that progressive low temperature stiffening of most elastomers upon prolonged storage is to be expected except in the case of interpolymers such as GR-S with a fairly large amount of each component. It seems likely that this progressive stiffening is due to crystallization, and it would be of interest to have had x-ray diagrams of the elastomers after short and long exposure to substantiate this point. The progressive stiffening of GR-I in spite of its being an interpolymer and in spite of the large amounts of low temperature plasticizer present indicates that the diene monomer is not present in sufficient amounts to interfere with the crystallization of the isobutylene component.

SUMMARY AND CONCLUSIONS

A new method for measuring the flexibility of rubber has been described. The method consists essentially in determining the stress-strain curve obtained by loading and unloading a loop formed from a one-inch by six-inch strip cut from a test slab. A coefficient of flexibility independent of the thickness of the sample and, in addition, information on per cent resilience were obtained.

By the use of the method described, the behavior of various natural and synthetic rubber gas mask facepiece compounds was studied during one month to three months' exposure at various temperatures down to -20°F . Progressive stiffening probably due to crystallization was found for natural rubber, GR-I, and GR-M compounds at low temperatures. No tendency to crystallize was noted for the GR-S compound. Of the crystallizable polymers GR-I was the most resistant, and GR-M the least resistant to stiffening during low temperature storage.

It is of course evident that different polymers have inherently different degrees of resistance to low temperatures.

Disregarding these inherent differences the work reported indicates that the resistance of elastomer compounds to stiffening during prolonged low temperature storage is favored by the following:

1. Use of interpolymers made from monomer mixtures having a relatively large proportion of each component, thus obtaining mutual interference with crystallization.
2. Use of a "tight" cure which probably so impedes the movement of the polymer chains as to make crystallization difficult.

ACKNOWLEDGMENT

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EFFECT OF IRON ON AGING OF GR-S*

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The harmful effects of copper and manganese on the aging of natural rubber are well recognized¹. Iron in some forms is known to be deleterious, but to a lesser extent than either copper or manganese¹. Iron pigments have been widely used in natural rubber, while copper and manganese contamination of rubber and compounding ingredients has been carefully avoided. Comparison of the effects produced by the acetylacetonates of copper, manganese, and iron on the rate of oxygen absorption of raw crepe natural rubber has shown iron to be the least active as a catalyst². Iron was found to be the least deleterious when ferric stearate, manganous oleate, and cupric stearate were compared in vulcanizate aging tests³.

Because iron is such a common material of construction, all rubber products can be contaminated readily by this metal during mixing and curing. Contamination of GR-S and finished products from it by iron is more likely than similar contamination of natural rubber because of the nature of the operations employed in the manufacture of the GR-S polymer. It was the object of this work to study the effect of iron contamination on the aging of GR-S polymer and vulcanizates and to compare the effect of iron on GR-S with that of copper and manganese.

DETERMINATION OF RESISTANCE OF GR-S POLYMER TO AGING

In evaluating the resistance of the GR-S polymer to accelerated aging, 50-gram samples were heated in a forced circulation oven held at 90°, 110°, or 120° C. During deterioration in the oven-aging test, a GR-S sample usually proceeds through definite stages of stiffening or cure and then starts to resinify. In some cases, there is an initial softening before this stiffening takes place. These stages of deterioration can be determined readily by visual and hand examination. In the earlier stages of stiffening or cure, where Mooney plasticities can be determined, the hand tests can be correlated with these plasticities.

During the artificial aging, the polymer samples were examined at the end of each day. The effect of natural aging on the condition of the polymer was determined by allowing samples to age one year at room temperature.

Preparation of polymer samples.—The laboratory polymer samples used in this investigation were prepared from uninhibited GR-S latex taken from a plant autoclave just before the addition of the stopping agent. A dispersion of the desired antioxidant was added to the latex and then coagulation was effected, usually by a 2 per cent aluminum sulfate solution. The coagulum was washed thoroughly in a laboratory mill and then dried 20 hours at 75° C.

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POLYMER AGING RESULTS

In Figure 1, the results of aging a series of polymer samples containing increasing percentages of iron are shown. In the preparation of these samples, the iron was added to the coagulant solution as ferric sulfate. The highest concentration of iron in the polymer which was investigated was that of a sample coagulated by ferric sulfate alone. In addition, a sample was prepared in which a relatively large amount of iron was added to the latex before coagulation as ferric oxide. All the samples were analyzed for iron by a colorimetric method based on the ferric thiocyanate complex⁴.

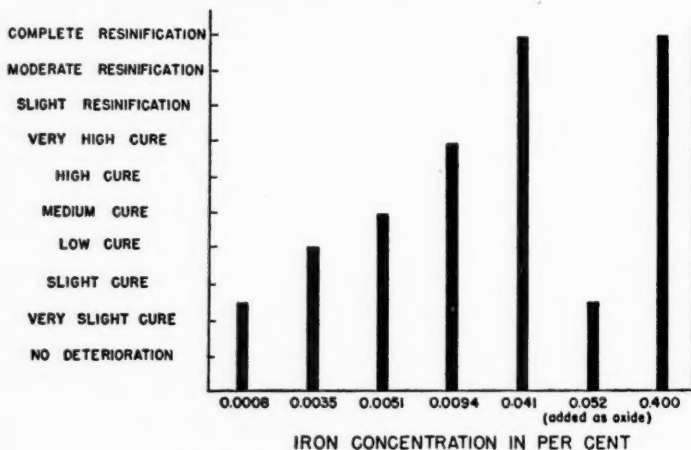


Fig. 1.—Effect of iron concentration on aging of GR-S polymer.
Antioxidant, 2 per cent phenyl- β -naphthylamine
Polymer samples aged 4 days at 110° C.

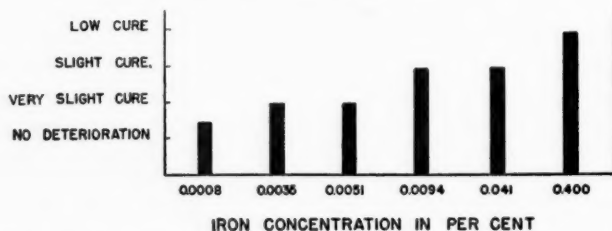


Fig. 2.—Effect of increasing iron concentration on condition of GR-S after one year of aging at room temperature.
Antioxidant, phenyl- β -naphthylamine

Figure 1 shows that, as the iron concentration in the polymer increases, the resistance of the polymer to deterioration in the accelerated aging test decreases. Iron added to the latex as the oxide did not affect the aging of the polymer. This emphasizes the fact that the iron must be present in the polymer in a soluble form to affect polymer aging. When added to the coagulant as ferric sulfate, it undoubtedly reacts during coagulation with the soap in GR-S latex to form polymer-soluble ferric salts of fat acids.

The effect of the concentration of iron on the natural aging of the polymer samples is shown in Figure 2. Although the effect of increasing iron concentra-

tions is not so great as in accelerated aging, the deleterious effect of iron is evident in these results.

The antioxidant employed in the samples of Figures 1 and 2 was phenyl- β -naphthylamine. Similar results were obtained when the polymer samples were protected by Santoflex-B (2,2,4-trimethyl-6-phenyl-1,2-dihydroquinoline), BLE (dimethylacridane), or Stalite (heptylated diphenylamine).

Figure 3 gives a comparison of the effect of iron with that of copper and manganese. These metals were added to the polymer by means of the coagulant to give the same increment of metal concentration (0.01 per cent). The results show that iron is more deleterious to the aging of the polymer than either copper or manganese. This is interesting in view of the fact that copper or manganese is more deleterious than iron in natural rubber.

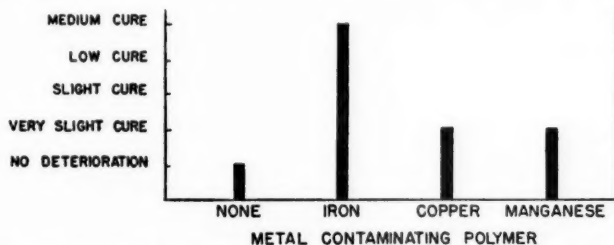


Fig. 3.—Comparison of effect of iron, copper, and manganese on GR-S polymer aging.

Antioxidant, 2 per cent phenyl- β -naphthylamine

Polymer samples oven-aged one day at 120° C

Metals added through coagulant to give concentration of 0.01 per cent

Aluminum sulfate is used as a coagulant for the commercial polymer designated as GR-S-AC, sometimes referred to as alum-coagulated GR-S. The grades of aluminum sulfate commercially available contain varying percentages of iron, those of higher iron content having been particularly prevalent during the war period. It therefore became of interest to compare as GR-S coagulants aluminum sulfate samples differing in iron content. In much of the following work, a low-iron aluminum sulfate sample is compared with a commercial grade of aluminum sulfate which has a higher iron content. The aluminum sulfate of higher iron content is referred to as commercial aluminum sulfate.

In Figure 4, a comparison is made between a GR-S sample coagulated with low-iron aluminum sulfate and a sample coagulated with commercial aluminum

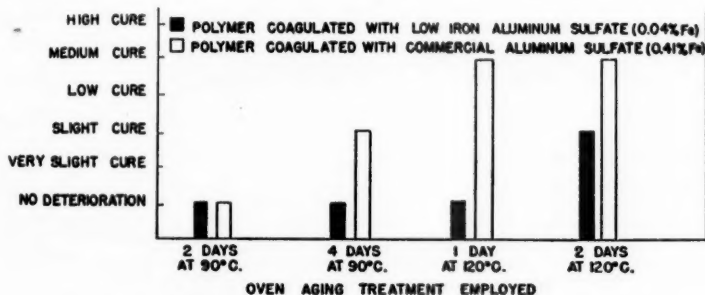


Fig. 4.—Commercial vs. low-iron aluminum sulfate in polymer aging test.

Antioxidant, 2 per cent phenyl- β -naphthylamine

sulfate. Although there is no apparent difference when the polymers are aged 2 days at 90° C, more drastic heat treatment, 4 days at 90° C or 1 or 2 days at 120° C, shows the low-iron aluminum sulfate GR-S to be superior.

The effect of the strength of the antioxidant employed on the difference between samples coagulated with commercial aluminum sulfate and with low-iron aluminum sulfate appears in Figure 5. These results indicate that a

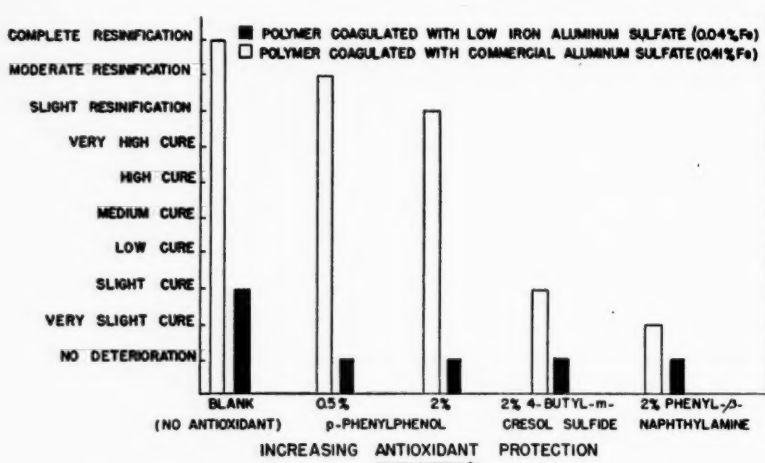


Fig. 5.—Effect of antioxidant on degree of difference between low-iron and commercial aluminum sulfate-coagulated samples.
Samples oven-aged 4 days at 90° C

strong antioxidant such as phenyl-β-naphthylamine minimizes the effect of the iron. When relatively weak antioxidants are employed, the degree of improvement obtained by using low-iron aluminum sulfate is pronounced. In the case of samples containing no antioxidant (blanks), the degree of improvement is the greatest. A blank coagulated with low-iron aluminum sulfate can be dried successfully and has fair to good resistance to oven aging at 90° C. On the other hand, a blank coagulated with commercial aluminum sulfate resinifies on drying 20 hours at 75° C.

When it is desirable to use antioxidants which are excellent from the standpoint of discoloration, low-iron aluminum sulfate can be substituted for com-

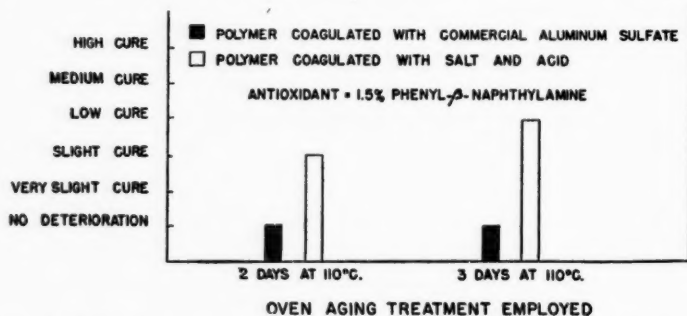


Fig. 6.—Salt-acid vs. commercial aluminum sulfate coagulation in polymer aging test.

mercial aluminum sulfate to good advantage. Since such antioxidants are relatively weak, the stability of the polymer can be improved considerably without sacrificing resistance to discoloration.

A comparison of a GR-S polymer coagulated with commercial aluminum sulfate and stabilized with phenyl- β -naphthylamine with a similar polymer coagulated with salt and acid (Figure 6) shows that the aluminum sulfate polymer is somewhat superior in aging resistance. Hence, even with some iron sulfate as an impurity, there appears to be some advantage in using aluminum sulfate for coagulation instead of salt and acid.

It appears from the above results that aluminum sulfate coagulation improves the stability of the GR-S polymer. This probably can be attributed to the presence of the aluminum salts of fatty acids which are formed by the reaction of the soap in GR-S latex with the aluminum sulfate coagulant. The relative stability of an aluminum sulfate-coagulated sample containing no antioxidant is evidence that these aluminum salts of fat acids have some protective effect. When salt-acid coagulation is employed, only fat acid appears in the polymer, and this protective effect of the aluminum salts of these fat acids is lost. The presence of iron salts in the coagulant solution results in the formation of iron salts of fat acids in the GR-S polymer along with the aluminum salts. These iron salts detract from the protective action of the aluminum salts, hence their removal from the coagulant results in improvement in aging. If the percentage of iron salt present is not very great, as in the case of commercial aluminum sulfate, the protective action of the aluminum salts of the fat acids which are formed in the GR-S polymer more than counterbalances the deleterious effect of the iron salts, and the net effect is some improvement in aging in comparison with a polymer which has been coagulated with salt and acid.

OXYGEN ABSORPTION STUDIES

The rate of oxygen absorption of GR-S polymers and vulcanizates has been studied by Shelton and Winn under the Firestone Fellowship at the Case School of Applied Science⁵. To them the authors are indebted for the oxygen absorption results presented in this paper.

The studies of the rate of oxygen absorption of GR-S polymer correlate very well with the polymer aging results. In Figure 7 a sample coagulated with low-iron aluminum sulfate is shown to absorb oxygen at a considerably slower rate than one coagulated with salt and acid. A sample of GR-S coagulated with commercial aluminum sulfate absorbed oxygen at a slower rate than the salt-acid coagulated sample, but at a faster rate than the low-iron aluminum sulfate sample.

Figure 8 shows that a sample coagulated with ferric sulfate absorbs oxygen at a much more rapid rate than a sample coagulated with reagent grade aluminum sulfate (containing less than 0.002 per cent iron). A mixture of 1 part of ferric sulfate and 12 parts of aluminum sulfate gave a polymer which absorbed oxygen at a somewhat slower rate than the ferric sulfate-coagulated sample.

The processing breakdown of natural rubber is known to involve oxidation of the rubber hydrocarbon⁶. The more rapid rate of oxygen absorption of salt-acid coagulated GR-S as compared with aluminum sulfate-coagulated GR-S correlates with the slightly greater ease of processing reported for the salt-acid polymer⁷. The high oxygen absorption of the high iron containing polymers reported here is in agreement with the use of ferric naphthenate as a polymer

softener and a processing aid for GR-S as reported by the British⁴. The use of ferric naphthenate as a softener is also understandable in view of the fact that in the polymer aging studies of this paper, it has been observed that the high-iron samples have a much greater tendency to go through an initial softening stage before stiffening, compared to the samples low in iron.

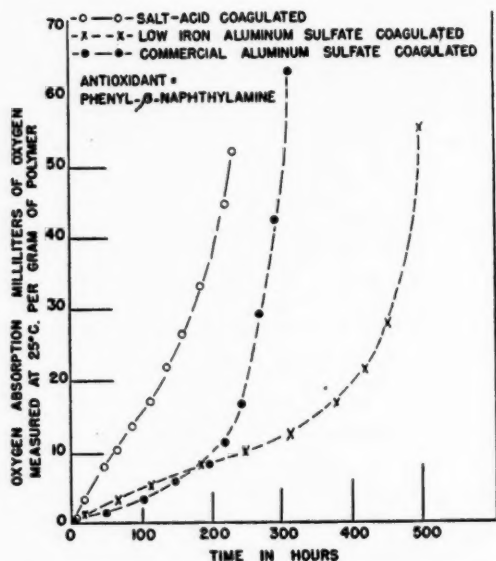


Fig. 7.—Effect of alum vs. salt-acid coagulation on rate of oxygen absorption. 100° C, 760 mm.

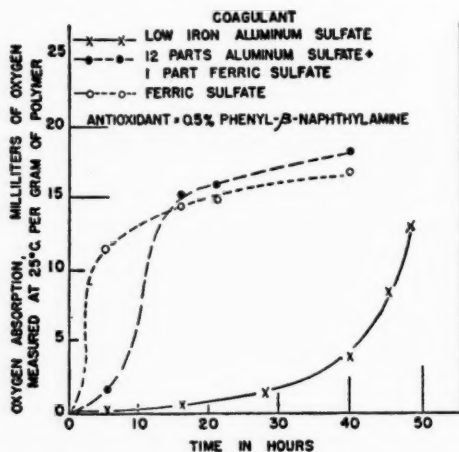


Fig. 8.—Effect of iron on rate of oxygen absorption of GR-S polymer. 100° C, 760 mm.

VULCANIZATE PREPARATION AND TESTING

In the study of the effect of iron on vulcanizate properties, many of the polymers prepared for the polymer aging tests were utilized. For this work the tread stocks in Table I were used. The tests which were carried out using these stocks are also indicated in Table I.

In the determination of tensile properties, four cures were employed: two undercures, an optimum cure, and an overcure.

Both air-bomb aged and oven-aged tensile properties were determined. The air-bomb conditions were 10 hours at 260° F, using a pressure of 60 pounds. Oven aging was carried out for 4 days at 212° F.

TABLE I
TEST STOCKS FOR STUDY OF EFFECT OF IRON ON GR-S
VULCANIZATE PROPERTIES AND OXYGEN ABSORPTION

	Stock 1	Stock 2
GR-S polymer	100.00	100.00
Pine tar	3.00	—
Stearic acid	3.00	1.00
Coal-tar softener	3.00	5.00
Zinc oxide	5.00	5.00
Channel black	50.00	50.00
Santocure	1.20	1.20
Sulfur	2.00	2.00
	167.20	164.20

Stock 1, cured at 280° F
Optimum cure, 80 minutes at 280° F

Test	Cure employed (min.)
Tensile properties	40, 60, 80, 120
Hot elongation	80
Blow-out time	80
Running temperature	80
Per cent rebound	80
Rate of groove cracking	80, 160

Stock 2, cured at 298° F
Oxygen absorption 50

In the case of tensile values, the percentage retention of the normal value after aging was calculated for each cure. To show the average effect of aging for the four cures employed, the retention percentages for these cures were averaged. In the graphs, the average value thus calculated is referred to as "average per cent retention of original property". Elongation values were handled in a similar manner.

For the 200 per cent modulus, the increase in modulus caused by aging was calculated for each cure. To show the overall effect on modulus for the cures employed, these modulus increases were averaged. The "average increase in modulus" thus obtained is plotted in the graphs.

The hot elongation was determined using rings having an inside diameter of 1 inch and an outside diameter of 1.37 inches, cut from slabs 0.075 inch thick. The optimum cure was employed in the preparation of the slabs. Four rings were used for each determination and the test temperatures were 100° and 200° F. The aged hot elongation was determined on vulcanizates which had

been heated in an oven for 5 days at 212° F. The per cent retention of hot elongation after aging was calculated in each case and these values were used for plotting.

VULCANIZATE TESTING RESULTS

Particularly at the higher concentrations tested, soluble iron had some accelerating effect on cure as judged by the normal tensile properties. Other than the effect that one might expect from slight cure acceleration, iron had little or no effect on running temperature, blow-out time, percentage rebound, unaged hot elongation, and rate of crack growth in unaged and aged samples. Hence these results are not presented in detail.

Iron was found to have some effect on the oven- and air-bomb aging of GR-S vulcanizates. Most of the following discussion is limited to air-bomb aging results, although somewhat similar results were obtained in oven aging.

In Figure 9, the average percentage retention of tensile and elongation and

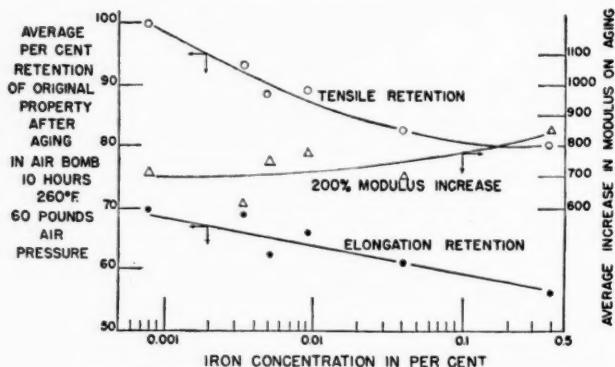


FIG. 9.—Effect of iron concentration on GR-S vulcanizate aging. Antioxidant, 2 per cent phenyl- β -naphthylamine

the average increase in modulus after air-bomb aging are plotted against iron concentration. As in the case of the polymer-aging study, the iron was added to the polymer through the coagulant solution as ferric sulfate. It is apparent that as the iron concentration increases, the average percentage retention of tensile and elongation decreases and the average increase in modulus becomes somewhat greater. However, these effects are not very pronounced even at high iron concentrations. Hence, iron does not have nearly as much effect on vulcanizate aging as on polymer aging.

The effect of iron concentration on the retention of hot elongation (measured at 100° and 200° F) after aging is shown in Figure 10. As in the case of normal elongation, increasing the iron concentration caused a decrease in the percentage retention of hot elongation after aging.

The results of Figures 9 and 10 were obtained with phenyl- β -naphthylamine as the antioxidant. Similar results were obtained when a GR-S polymer stabilized with Santoflex-B, BLE, or Stalite was used for the preparation of the vulcanizates.

The effect of iron on the average percentage retention of tensile and elongation and on the increase in modulus is compared with that of copper and manganese in Figure 11. These metals were added to the polymer through the

coagulant solution as the corresponding sulfates to give a concentration of 0.01 per cent of metal, based on the polymer. The results show that, while the presence of iron slightly reduces the average percentage retention of tensile and elongation, copper or manganese has little effect. None of these metals affected the average increase in modulus on aging.

In view of the fact that, in natural rubber, copper and manganese have been observed to be more harmful than iron, the above results are of particular interest. In the case of GR-S, it has been shown in this work that iron is more harmful than either copper or manganese in both polymer and vulcanizate aging tests.

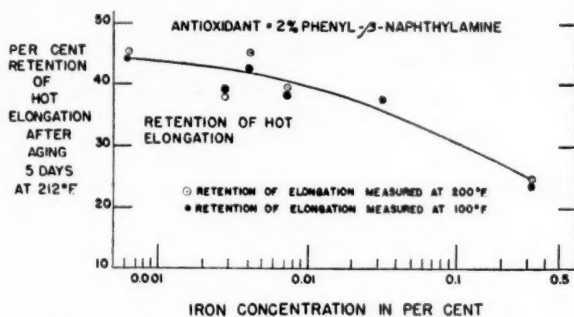


Fig. 10.—Effect of iron concentration on aged hot elongation.

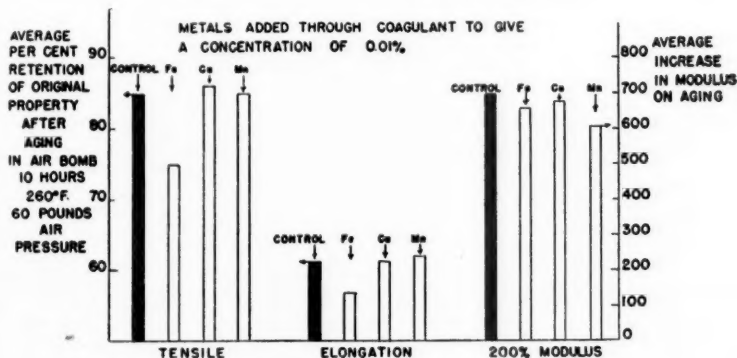


Fig. 11.—Effect of iron, copper, and manganese on GR-S vulcanizate aging. Antioxidant, 2 per cent phenyl-β-naphthylamine

The fact that the aging of a vulcanizate from a polymer coagulated with commercial aluminum sulfate can be improved somewhat by substitution of low-iron aluminum sulfate is shown in Figure 12. The improvement is in the average percentage retention of both tensile strength and elongation. The average increase in modulus was not affected by this change. Similar results were obtained in Figure 13, where the above comparison is made using the oven-aging test instead of air-bomb aging. A comparison of Figure 12 and Figure 13 illustrates the similarity of the results of air-bomb aging and those obtained by oven aging.

The above results all point to the fact that iron does not have so great an effect on vulcanizate aging as on polymer aging. A possible explanation which may be advanced is that the vulcanizate structure may be more resistant to the

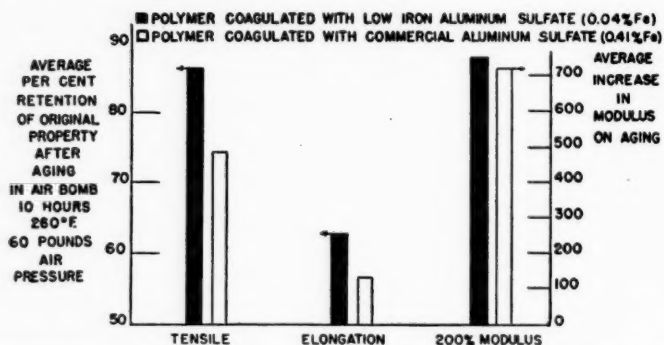


Fig. 12.—Air-bomb aging of vulcanizates from GR-S coagulated with commercial and low-iron aluminum sulfate.

Antioxidant, 2 per cent phenyl- β -naphthylamine

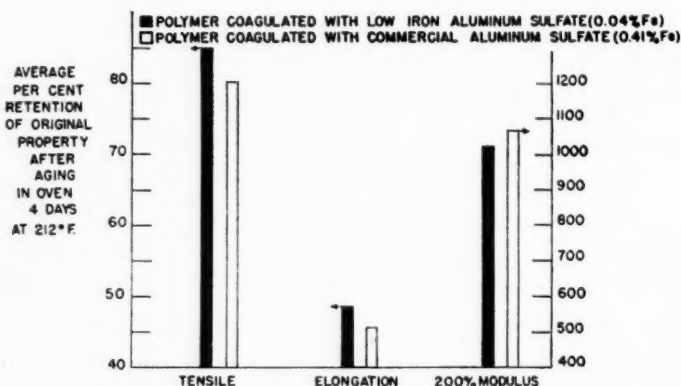


Fig. 13.—Oven aging of vulcanizates from GR-S coagulated with commercial and low-iron aluminum sulfate.

Antioxidant, 2 per cent phenyl- β -naphthylamine

catalysis of oxygen attack on GR-S polymer shown by iron salts, the active points of attack for oxygen along the synthetic rubber hydrocarbon chain having been at least partially substituted or reacted during vulcanization. Another possibility is that the iron salts may be destroyed to a large extent during curing by chemical reaction to form iron sulfide. In the latter insoluble form, iron would not be expected to have much effect on aging.

Studies on the rate of oxygen absorption of GR-S vulcanizates showed good correlation with vulcanizate aging results. In Figure 14, it is shown that a low-iron aluminum sulfate vulcanizate absorbs oxygen at only a slightly lower rate than a vulcanizate from a GR-S polymer prepared with commercial aluminum sulfate. The latter gave a very slightly lower rate of oxygen absorption than a vulcanizate from a salt-acid polymer.

Figure 15 shows that vulcanizates from polymers coagulated with ferric sulfate or a mixture of 1 part of ferric sulfate and 12 parts of aluminum sulfate absorb oxygen at a faster rate than a vulcanizate from a polymer coagulated with low-iron aluminum sulfate. Here the degree of difference is magnified by using relatively large percentages of iron and a low antioxidant concentration.

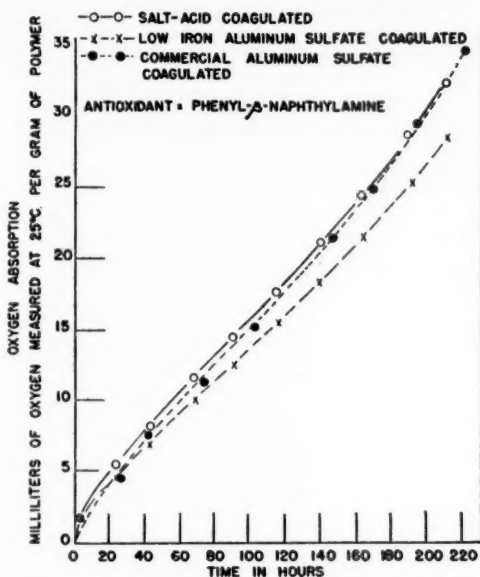


Fig. 14.—Rate of oxygen absorption of alum and salt-acid GR-S vulcanizates. 100° C, 760 mm.

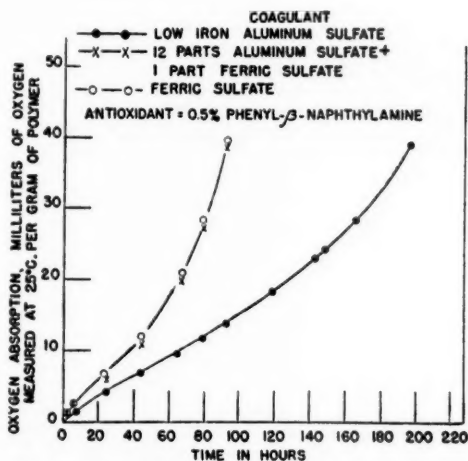


Fig. 15.—Effect of iron on rate of oxygen absorption of GR-S vulcanizates. 100° C, 760 mm.

The aging and oxygen absorption results on GR-S polymers and vulcanizates point to the fact that only small percentages of soluble iron can be tolerated in applications where aging of the polymer is important. For applications which involve the use of relatively weak nondiscoloring antioxidants the elimination of soluble iron contamination is particularly important. From a vulcanizate aging standpoint, contamination by small percentages of iron is not serious but large percentages of soluble iron should be avoided.

CONCLUSIONS

Soluble iron decreases the resistance of the GR-S polymer to aging. The effect of iron is greater than that of copper or manganese.

The aging of an aluminum sulfate-coagulated polymer can be improved by the use of low-iron aluminum sulfate instead of the commercial grade of this material. The use of commercial aluminum sulfate as a coagulant gives a polymer somewhat superior in aging to one coagulated with salt and acid.

The aging of GR-S vulcanizates is accelerated slightly by polymer-soluble iron. Relatively high iron concentrations are required to produce much effect. The effect of iron on vulcanizate aging is much less than in the case of polymer aging.

The presence of iron increases the rate of oxygen absorption of GR-S polymer and vulcanizates, the effect being less in the latter case. The rate of oxygen absorption of aluminum sulfate-coagulated GR-S polymer is decreased by employing low-iron aluminum sulfate instead of the commercial grade. A polymer coagulated by commercial aluminum sulfate absorbs oxygen at a slower rate than one coagulated by salt and acid.

ACKNOWLEDGMENT

Acknowledgment is made of the valuable oxygen absorption data supplied by J. Reid Shelton and Hugh Winn of the Case School of Applied Science.

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HIGH-SOLIDS SYNTHETIC LATEX DIRECTLY FROM REACTOR *

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In the ten-year period preceding the outbreak of hostilities with Japan, imports of natural latex into the United States assumed a sharply rising trend. (Figure 1 shows that the 1940 figure is somewhat high owing to the inception of stockpiling.) Roughly 80 per cent of this latex was shipped in as a concentrate of 60-65 per cent solids, since this eliminated shipping excess water originally present in the latex, and constituted a material suitable for various applications in which the normal latex could not be used.

Although small quantities of special-purpose synthetic latices had been produced domestically before 1941, it was not until 1944 that substantial production of a general-purpose synthetic latex got under way (Figure 1). With this production, there arose the problem of producing a concentrate for use in applications where a high-solids latex is essential. Natural rubber latex can be concentrated readily, either by centrifuge or a creaming process, since it has a large particle size. Synthetic rubber latex, on the contrary, has a very small particle size, which makes concentration a more difficult and costly operation. In practical creaming operations a significant amount of polymer is usually lost in the serum.

This article presents a description of two new synthetic latices made to 55-60 per cent solids directly in the reactor and a short description of the methods of preparation. Since the production of these high-solids latices is only slightly more expensive than the production of low-solids types, they can be sold at only a small increase in cost over the latter.

PLANT EQUIPMENT CHANGES

In the production of high-solids latices several problems were encountered. The more troublesome were: (1) high viscosity and gelation of the latex, (2) high rate of heat evolution, (3) dying out of the reaction, and (4) difficulty in stripping because of foaming.

During the reaction the latex goes through a period of high viscosity, which may cause gelation of the entire mass of latex in the reactor. This creates a serious heat-transfer problem in removal of the heat of polymerization. The problem is further complicated by the large proportion of monomers in the reactor batch, which necessitates the removal of a much larger total amount of heat than for type III latex taken to only 38 per cent solids.

The plant reactor installation worked out to overcome the foregoing difficulties is shown in Figure 2. To circulate the viscous latex, the standard reactor agitators were replaced with duplex open-tilted Turbo impellers, in accordance

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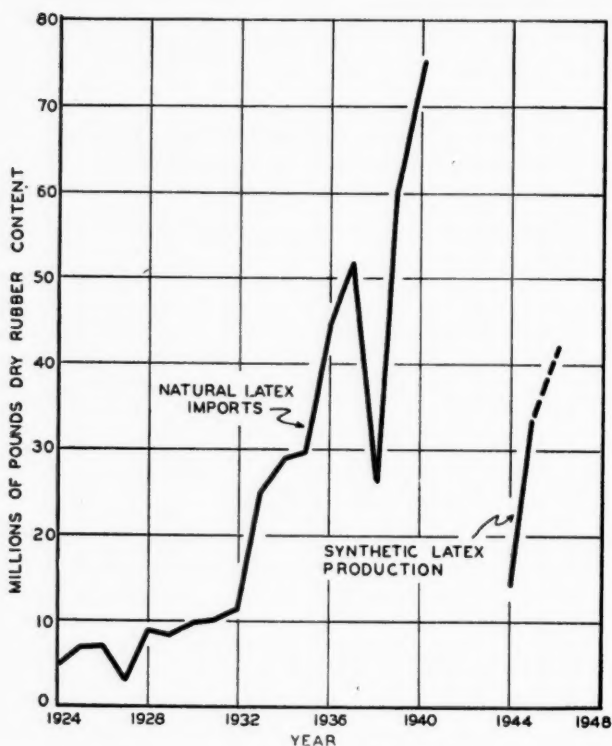


Fig. 1.—Latex usage in the United States.

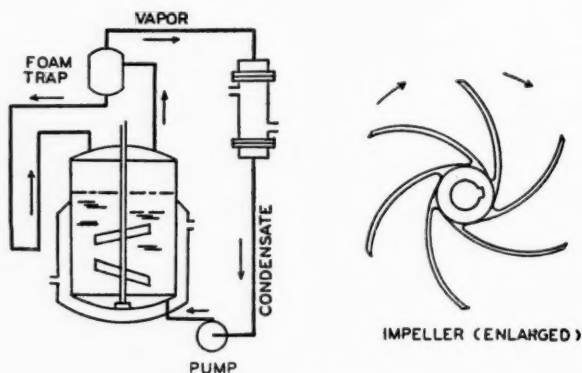


Fig. 2.—Schematic diagram of reactor installation.

with the recommendations of the Turbo-Mixer Corporation. This type of agitator was found to produce good circulation of the viscous material with moderate power consumption. The maximum power consumption thus far observed on a 3000-gallon reactor installation is 11 horsepower.

The method devised for removal of the excess heat of reaction is also shown in Figure 2. Each reactor is provided with a vapor line, a condenser, and a liquid butadiene recycle pump. The reactor batch is cooled by the vaporization of butadiene, which is then condensed and recycled back into the reactor. The recycled butadiene is introduced at the eye of the bottom impeller where it is intimately mixed with the latex, and, passing up through, produces a honeycombed structure more readily circulated by the agitators. Temperature control is further facilitated by reducing the rate of heat evolution by modifying the charge formula to give a slower and more uniform rate of reaction than normally is obtained in type II or type III latex. It was found also that the same changes in formulation eliminated dying out of the reaction.

Excessive foaming during steam stripping (to remove small amounts of unreacted monomers) presented an extremely difficult problem. Recent development work on new defoamers has pointed to the possibility of stripping these high-solids latices successfully.

The end result of these changes is a slow easily controlled reaction to high conversion and high solids. Work with the reflux condenser has been limited up to the present time. It is now indicated that this installation will handle considerably faster reactions; this makes possible reactor efficiencies (pounds of polymer per cubic foot reactor volume per hour) equal to or better than those for low-solids latices.

Thus far the techniques described have been used for the preparation of latices of two butadiene/styrene ratios: 75/25 (similar to type II) and 50/50 (similar to type III).

55-60 PER CENT SOLIDS TYPE III LATEX

Type III is the general-purpose high-styrene latex employed where good gum tensile properties are required. The formulation of the high-solids latex differed somewhat from that of standard type III latex. To obtain high solids content, the water was reduced 50 per cent. The amount of soap also was reduced considerably, and an auxiliary stabilizer (the sodium salt of an alkaryl sulfonate) was incorporated.

Type III latex is usually reacted to about 90 per cent conversion, after which the unreacted monomers are stripped off. However, since high-solids latex is difficult to strip, it was reacted to high conversion (usually 95 per cent or higher) to reduce residual monomer content.

The high-solids polymerization was carried out at 140° F, whereas normal type III latex is polymerized at 150° F. To maintain better control of the increased heat of reaction liberated in the high-solids polymerization, the reaction time was deliberately increased from 18 to 46 hours. (The reaction rate can be varied within wide limits by adjusting the ratio of soap to auxiliary stabilizer.)

Table I presents a comparison of the properties of finished normal type III latex and high-solids latex. The high-solids latex contains slightly more styrene in the polymer than is actually present in the initial charge. This appears to be due to the formation of a small amount of butadiene dimer during polymerization; this increases slightly the proportion of styrene in the charge. (The difference between the percentage of total free unsaturates and the percentage of free styrene is believed to be largely butadiene dimer.) A butadiene-styrene latex carried to high conversion always contains more styrene in the polymer than does a latex with the same monomer charge ratio made to a lower

TABLE I
PROPERTIES OF FINISHED TYPE III LATICES

Tests	Normal type III	High-solids type
Total solids (%)	38.1	56.4
Mooney viscosity (4 min.)	80	98
Styrene in polymer (%)	47.9	45.1
Free unsaturates ^a (%)	0.20	0.90
Free styrene (%)	0.06	0.49
Average particle diameter (Å. U.)	1125	2130
Viscosity (conical) (cp.)	7.3	75.6
Yield point (conical) (cg. per sq. cm.)	0.08	3.1
Maron stability test (% coagulum)	8.3	Nil

^a Bromide-bromate method. Calculated as styrene.

conversion. This results from the fact that, in a copolymerization, the reaction rate of butadiene is greater than that of styrene¹. That is, the alpha coefficient, the ratio of the reaction rate constant of butadiene to that of styrene, is greater than unity. Hence, polymer increments formed early in the reaction are rich in butadiene. As a corollary, increments formed late in the reaction are rich in styrene since, at this point, a disproportionately large amount of the butadiene has already polymerized.

Table I illustrates the important fact that the average particle size of the 55-60 per cent solids latex is almost twice that of the standard type III latex. The increased particle size results in greatly improved drying properties in the high-solids latex.

The viscosity and yield point values given in Table I are for an individual batch. The blending of several batches of high-solids latices, as is the usual plant practice, reduces the viscosity and yield point values for the blend to approximately one half of the predicted, weighted average value. Thus a viscosity of 40 centipoises and a yield point of 1.5 cg. per square centimeter would be more truly representative of the flow characteristics to be expected from the high-solids latex. The only explanation offered to date for this marked reduction is that the particle size distribution for a blend probably approaches the ideal more closely, and gives lower viscosity and yield point for the same solids content.

The solids shown in the tables were determined by the standard method for concentrated latices² and Mooney viscosity was determined by the procedure published by Mooney³. The styrene content of the polymer was obtained by measuring the refractive index of the polymer after extraction with solvent (to remove nonhydrocarbon material). Free unsaturates of the finished latices were measured by a bromide-bromate titration, whereas free styrene determinations were made by an ultraviolet absorption test. Average particle diameter was determined by a light-scattering method based on relations derived by Debye⁴. Viscosity and yield point of latex were measured by published methods⁵.

The Maron stability test is a measure of the stability of latex toward rubbing. It was devised by Maron of Case School of Applied Science and was originally intended for measuring mechanical stability of type II latex which, because of its small particle size, does not coagulate in the Hamilton-Beach test. Subsequently, it has been found to be an excellent test for larger-particle latices also. It is carried out in a metal cup equipped with a tightly fitting sheet of cured rubber in the bottom. Seventy-five grams of the latex are poured

into the cup, and a stainless steel disk, 2 inches in diameter and having shallow grooves cut in the bottom face, is lowered into the cup until it lightly touches the sheet of rubber in the bottom. Under these conditions the disk is rotated at 1000 revolutions per minute for 3 minutes. The latex is then poured through cheesecloth to strain out the coagulum which is dried, weighed, and reported as a percentage of the rubber originally present in the latex sample. As will be seen from Table I, the 55-60 per cent solids latex possesses excellent rubbing stability.

Table II illustrates typical cured film properties for high-solids latex and for creamed type III latex. (It is difficult to lay a satisfactory film from an unconcentrated type III latex.) Except for a slightly lower elongation of the high-solids latex, the properties are substantially equivalent. Film evaluations were made by the method described by Peaker⁶.

TABLE II
PROPERTIES OF CURED FILMS

Oven cure at 100° C (min.)	Normal type III		High solids type	
	Tensile ^a (lb. per sq. in.)	Elongation ^a (%)	Tensile (lb. per sq. in.)	Elongation (%)
15	2100	870	2100	700
30	2200	740	2400	720
60	2500	700	2300	600
120	2200	670	2000	520

^a Results given are for film laid from creamed standard type III latex.

55-60 PER CENT SOLIDS TYPE II LATEX

Thus far this discussion has been confined to high-solids latex with a butadiene-styrene ratio comparable to type III. A second high-solids latex with a monomer ratio comparable to that of type II also has been produced. The polymer in type II latex is substantially identical with GR-S, except that no antioxidant has been added. This type of polymer is used where good gum tensile values are not important when compared with such other properties as cold resistance, etc. The same general formulation was used in the high-solids type II latex as in the high-solids type III. Rosin soap was used as the emulsifier in the high-solids latex to obtain a lower viscosity in the finished latex than that obtained when fat acid soap is used. It was found possible to reduce the emulsifier and stabilizer content of the high-solids type II formula; this resulted in a lower nonrubber solids content. Also, by reducing the water content somewhat, a high total solids content was obtained.

Standard type II latex is run at a relatively low reaction temperature and to relatively low conversion compared with standard type III. High-solids type II latex, on the other hand, is run at the same temperature as high-solids type III and to the same high conversion, stripping of residual monomers thus being avoided.

Table III presents a comparison of the finished latex properties for normal type II and for 55-60 per cent solids type II latex. It will be seen again that the high-solids latex has a far larger particle size. Also, even before blending, the high-solids sample had a very low viscosity, which indicates excellent particle size distribution. The rubbing stability, as shown by the Maron test, is also excellent.

TABLE III
PROPERTIES OF FINISHED TYPE II LATICES

Tests	Normal type II	High-solids type
Total solids (%)	28.8	57.2
Mooney viscosity (4 min.)	50	78
Styrene in polymer (%)	24.3	25.0
Free unsaturates ^a (%)	0.2	0.58
Free styrene (%)	0.09	0.37
Average particle diameter (Å. U.)	925	2080
Viscosity (conicylindrical) (cp.)	8.0	17.5
Yield point (conicylindrical) (cg. per sq. cm.)	0	2.4
Maron stability test (%) coagulum	Nil	Nil

^a Bromide-bromate method. Calculated as styrene.

Although the two latices described are now available on a large scale basis, continuing development work indicates that further improvements can be introduced in the future. Recent work has shown that, for applications where it may be desirable, 55–60 per cent solids type II latex can be made with a considerably reduced nonrubber solids content compared with the present formula. It is believed that this reduction can be applied also to high-solids type III latex.

Up to the present time it has been necessary for the consumer to pay a considerable premium for concentrated latices. The successful development of high-solids latices produced in the reactor will practically eliminate this premium and furnish a material equal in quality to creamed latices.

ACKNOWLEDGMENT

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BASIC REACTIONS OCCURRING DURING RUBBER RECLAIMING. I. THE INFLUENCE OF RECLAIMING MEDIA, ANTIOXIDANT, AND DEFIBERING AGENTS ON VULCANIZED NATURAL RUBBER AT 195 POUNDS PER SQUARE INCH GAUGE PRESSURE (196.6° C) *

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The art of rubber reclaiming has been practiced for several decades. Comparatively little is known, however, about the reactions occurring during this process. Although the reclaiming of rubber is hardly ever carried out without the aid of reclaiming oils or defibering chemicals, it appeared desirable to study first the basic effects which the surrounding medium, antioxidant, or defibering agents at a temperature of 196.6° C (steam pressure, gage, 195 lbs. per sq. in.) exert on the rubber hydrocarbon before attempting to explain the action of reclaiming oils or chemicals. All experiments, therefore, described in the present investigation were carried out in the absence of reclaiming oils.

In general, all reclaiming processes depend on the expenditure of energy by one or the other means. Inasmuch as under prevailing conditions the least expensive supply is thermal energy and the most economical means of supplying thermal energy is steam, the greatest volume production of reclaim today is based on the application of steam in one way or another. Two processes are mainly used for this purpose. The heater, or pan process, is carried out in a single-shell autoclave, which permits direct contact of steam with the ground scrap. The digester process is usually carried out in a jacketed autoclave; the scrap is dispersed in water or in the solutions of the defibering agents, but is not in direct contact with live steam.

The scrap which ordinarily enters the reclaiming factory consists of a conglomerate of rubber compounds, badly contaminated with foreign material and partly oxidized. As such, it does not lend itself well to basic studies of any kind of reaction. Furthermore the difficulties encountered because of the insolubility of the reclaim and the means of analysis at our disposal today made it preferable to study a laboratory prepared pure-gum compound at first. This compound was so chosen that it could later be built into a tire compound. Fillers could be expected to have an influence on the rate of the reclaiming reactions rather than on the course of these reactions. It is fully realized, however, that scrap obtained from rubber goods which have been subjected to use before reclamation cannot be fully identical in its rate of reaction in comparison with the laboratory prepared compound.

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EXPERIMENTAL DETAILS

The formula for the basic pure-gum compound used, the milling and vulcanization conditions, and some physical and chemical properties are given below and in Table 1.

This vulcanized compound was ground on the mill and heated for various time intervals in the heater and in the digester at the 196.6° C (temperature equivalent to 195 lbs. per sq. in. steam gauge pressure.) The digester reclaiming was carried out in the presence of water-alkali, or metallic chloride solutions. The strength of the alkali and metallic chloride solutions was within the limits of concentrations generally used in the production of reclaim.

PURE-GUM BASIC COMPOUND

100	Smoked sheet rubber
5	Zinc oxide
3	Sulfur
1	Mercaptobenzothiazole
1	Stearic acid

Mill temperature: 140° F. Vulcanization at 270° F yielded an optimum tensile strength of 3000 lbs. per sq. in. at 660 per cent elongation.

TABLE 1
CHEMICAL PROPERTIES OF SMOKED SHEET AND VULCANIZED
BASIC COMPOUND

	Percentage
Acetone extract of the crude smoked sheet	2.75
Unsaturation of the crude smoked sheet ¹	91.2
Unsaturation of the vulcanized compound	86.7
Combined sulfur of the vulcanized compound	2.6
Free sulfur of the vulcanized compound	0.7
Acetone extract of the vulcanized compound	5.3
Chloroform extract of the vulcanized compound	0.6

After reclaiming, the digester treated scrap was thoroughly washed to a pH of 7; all reclaims were dried at room temperature for 24 hours and then dried to constant weight in a vacuum, and also at room temperature. They were given 10 passes on a cold and tight mill (setting 0.01 inch) and again subjected to vacuum for three days before analyses were carried out.

Acetone and chloroform extracts² were determined, as well as the unsaturation in the reclaim and the chloroform extracts. The time interval which elapsed between actual heater or digester treatment and analysis of the reclaim was about three weeks.

It was found that the grinding of the vulcanized compound did not have any effect on its unsaturation value or chloroform extract, nor did the initial air drying of the reclaim. Drying at elevated temperatures was avoided because the variable conditions existing during the drying interval in production, such as moisture and oxygen content, cannot be easily duplicated.

The modified Wijs method¹ was used for the determination of the unsaturation values. The shortcomings of the Wijs method were fully realized; however, the results obtained in this way would at least be considered from a comparative point of view. Inasmuch as the acetone extract was found to vary widely with the method of reclaiming and could be expected to change on addition of various materials to the original compound or scrap, the values obtained for the unsaturation, as well as for the chloroform extract of the reclaims, were recalculated, correcting for the acetone extractable matter.

The unsaturation of the reclaim was determined on the acetone-extracted sample, and all data on chloroform extracts refer to the chloroform extract of the reclaim before its revulcanization.

EXPERIMENTAL RESULTS

It had been previously established that proper results in the determination of unsaturation values by the Wijs method could be obtained even if the rubber sample did not dissolve in *p*-dichlorobenzene, and that the time of heating in *p*-dichlorobenzene could be extended up to six hours without affecting the results³. The reclaim did not dissolve in *p*-dichlorobenzene, but it dispersed. In an effort to obtain solution, heating for different periods of time was tried. Solution could not be obtained, even if the heating in *p*-dichlorobenzene was carried beyond six hours. No change in the value obtained for the unsaturation seemed to occur between one hour and two hours of heating. It was noticed, however, that the unsaturation value of the reclaim decreased considerably when the heating was carried to six hours (Figure 1). Inasmuch as

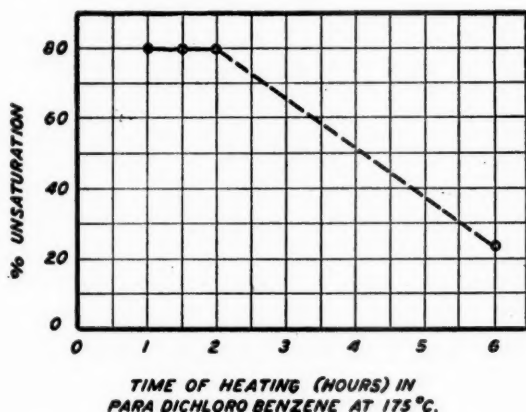


Fig. 1.—Effect of time of heating reclaimed rubber sample in *p*-dichlorobenzene on unsaturation value.

we were interested only in the application of this method to the determination of the unsaturation value of reclaim under varying conditions of processing, no further points were determined between two and six hours of heating. The value recorded for six hours of heating was obtained as a result of multiple determinations on different samples. In consideration of the above it was felt that a heating time of 1½ hours would be adequate for the purpose.

It was found also that the thickness of the reclaim sheet subjected to analysis for unsaturation was of major importance. Figure 2 shows that an average sheet thickness up to 0.005 inch was appropriate. An increase in the thickness of the sheet invariably caused a decrease in the unsaturation values.

Although the original compound contained 0.7 per cent of free sulfur at the peak of its physical properties, analysis of the heater and digester reclaims showed that all of the free sulfur was combined during the first 20 to 30 minutes of reclaiming except in the case of caustic digestions, where about 60 per cent of the free sulfur was solubilized during this time.

Previous investigators⁴ have studied the changes in combined sulfur that occur during the alkali reclaiming process and in the presence of asphalt. Asphalt can be used as a reclaiming agent, but it also reacts with sulfur and sometimes contains sulfur. Therefore it would be difficult to draw any conclusion from the work with regard to the effect of the alkali in the absence of asphalt.

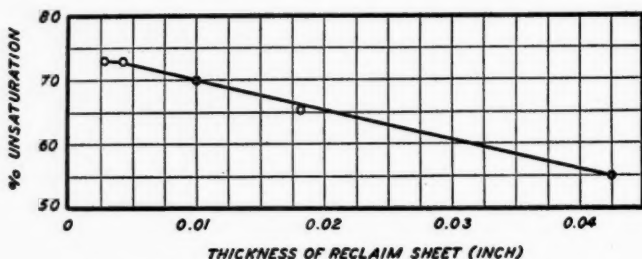


FIG. 2.—Effect of thickness of sample on unsaturation value.

Actually the two reactions which occur in the alkali process, solubilization of the free sulfur and the latter's combination with the rubber due to the temperature (196.6° C), counteract each other. It is interesting to note, however, that the reactions appear to be completed within the first 20 to 30 minutes of the reclaiming process and that the part of the sulfur which dissolves in alkali and is present as sodium sulfide does not react with the rubber even if the latter is exposed to it for as long as 16 hours at that temperature.

EFFECT OF SURROUNDING MEDIUM AND TIME

Figure 3 shows the effect of a live steam or water medium surrounding the scrap during reclaiming on the unsaturation value of the reclaim produced. No change in unsaturation value can be noticed over a period of 16 hours if the scrap is reclaimed while submersed in water (digester process). However, if the sample is heated in live steam (heater or pan process) a progressive decrease in unsaturation value, even if small, occurs after nine hours of heating.

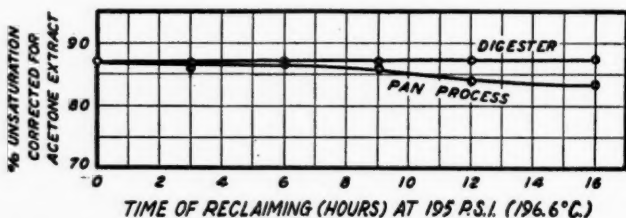


FIG. 3.—Effect of live steam heater or pan process and water-digester process on the unsaturation value of the reclaimed rubber.

These heater reclaims during intervals up to nine hours show a much greater increase in the acetone extract than the digester water treated reclaims (Figure 4). A decrease in the acetone extract of heater reclaim can be noticed if the reclaiming period is extended beyond nine hours. Similar results had been noticed previously⁵ in the study of reclaims prepared by the use of pine-tar oil. However pine-tar oil can affect the formation of the acetone extractable

substances from rubber; it is also soluble in acetone, and last, but not least, it is removed in part from the reclaim on release of pressure (steam distillation effect). Therefore it would be difficult to state what part of the acetone extract is due to the formation of acetone extractable substances from the rubber, and whether such formation is enhanced or decreased by the use of the oil.

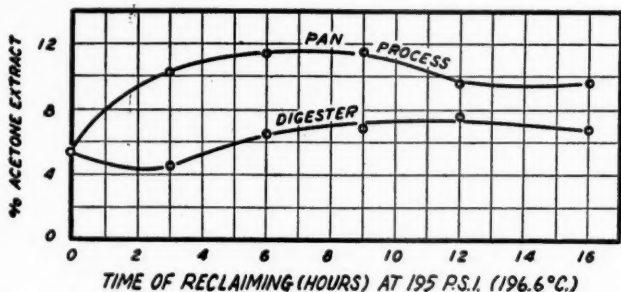


FIG. 4.—Effect of pan and digester processes on acetone extract of the reclaimed rubber.

The digester reclaim shows a small decrease in the acetone extract at reclaiming periods of three hours. This decrease can be considered a consequence of the solubilization of some of the foreign substances in the crude rubber, such as sugars, proteins, etc. Hot-water extraction of crude rubbers has been shown to solubilize part of these substances, and the decrease of the acetone extract found in this work corresponds to that traceable to such solubilization⁶. The total amount of acetone extract was found to be much smaller for water digester-process reclaiming than for pan-process reclaiming.

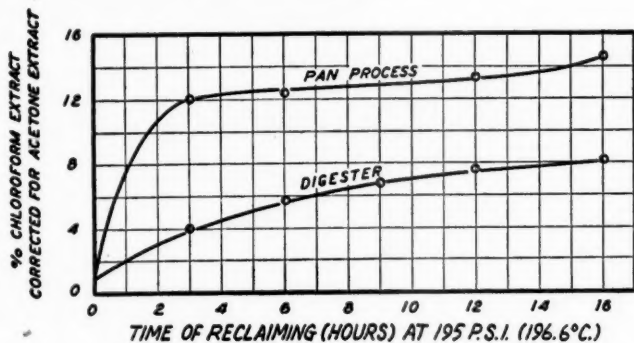


FIG. 5.—Effect of pan and digester processes on chloroform extract of the reclaimed rubber.

Figure 5 records the chloroform extracts from the two kinds of reclaim. Heater-process reclaim shows a great change in its chloroform extract during the first three hours of reclaiming, followed by a slow increase for longer periods of treatment. The reclaim treated in the digester, while submerged in water, exhibits a much smaller chloroform extract and a fairly uniform rate of increase over the whole period investigated. It should be remembered that the chloroform and acetone extracts, as obtained throughout this investigation, are entirely a function of the reclaiming reactions and are not due to the

addition of reclaiming oils. Tube reclaim prepared by the addition of pine-tar oil and caustic, but heated in open steam, had likewise shown a high rate of chloroform extract formation during the first hours of the reclaiming period⁷. The data obtained by these investigators⁵ were identical in trend with those obtained for the heater process in the present study.

The chloroform extracts obtained from the open-steam heater process and the water digester process reclaims were analyzed for unsaturation values. Complete solution of these extracts was obtained after ten minutes' heating in *p*-dichlorobenzene. It was found that the chloroform extracts of the nine- and twelve-hour heater-process reclaim were as high in unsaturation values as the original vulcanized compound from which the reclaim had been prepared. The unsaturation values of the chloroform extracts of the reclaims treated for nine and twelve hours in the digester were approximately 5 per cent less than those of the original compound or the respective reclaim prepared from it.

EFFECT OF DEFIBERING AGENTS

The chemical defibering agents in practical use today (just as forty years ago) are solutions of alkali, or metallic chlorides, such as calcium, zinc, and aluminum chlorides. In the present study both a solution of an alkali and a metallic chloride were used in the proportions ordinarily applied in whole-tire reclaiming at 195° C. However, inasmuch as fillers were not present in the compound used here, the amounts of the defibering agents generally used were recalculated on the basis of the rubber present in the tires, ordinarily subjected to reclaiming.

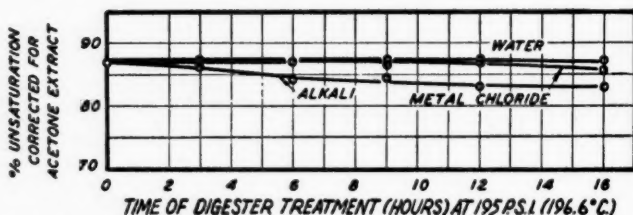


Fig. 6.—Unsaturation value of the reclaimed rubber produced when different defibering agents are used.

The practical differences in the behavior of alkali and so-called neutral metallic chloride reclaims have long been known to the reclaimer. Inasmuch as the cellulosic materials and decomposition products, as well as almost all of the alkali and metallic chlorides, are removed from the reclaim, such differences must be considered as being inherent to the reclaim prepared by each method and as resulting from the action of the defibering agents on the rubber hydrocarbon during the reclaiming procedure.

Figure 6 shows the effect of different defibering agents on the unsaturation values of the reclaim produced. Whereas the unsaturation values for the metallic chloride digester-treated reclaim are almost identical with those of the water digester-treated reclaim, a decrease in the unsaturation values for the alkali digester-treated reclaim can be noticed after three hours.

Equally parallel and almost identical in the general trend are the acetone extracts of the water and the metallic chloride digester-treated reclaims (Figure 7). The decrease in the acetone extract noticed for short periods of

water digester reclaiming cannot be noticed for the metallic-chloride digester reclaiming. This is probably due to the formation of insoluble salts, which prevent the solubilization of the foreign substances in the rubber. The value of the acetone extract of the alkali-treated reclaim drops far below the value of that found in the original compound. It should be remembered that these reclaims were washed exhaustively before analysis. The presence of alkali during reclaiming causes the formation of soluble soaps, which are removed during washing. These low acetone extract values are not found in industrial reclaiming because washing cannot be carried so far as in the laboratory.

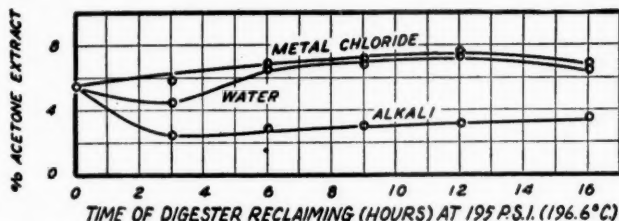


Fig. 7.—Acetone extract values of the reclaimed rubber produced when different defibering agents are used.

The chloroform extract values (Figure 8) also show considerable similarity between those obtained for the water and those for the metallic chloride reclaims. The unsaturation values of the chloroform extracts of these reclaims (9 and 12 hours) are about 5 per cent lower than those of the reclaims from which they are extracted or the unsaturation value of the original compound. The alkali reclaim exhibits much higher amounts of chloroform extract. The unsaturation values of the extract (9 and 12 hours) equal that of the original

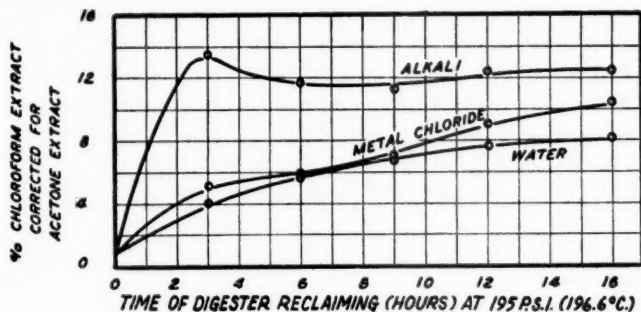


Fig. 8.—Chloroform extract values of the reclaimed rubber produced when different defibering agents are used.

compound, and the rate of increase of chloroform extract in this alkali reclaim reaches its peak within the first three hours. Very little change can be observed in the alkali reclaim chloroform extract after that time; whereas the metallic chloride and the water reclaims show a much steadier increase in chloroform extract over the whole period investigated. It could also be noticed that the depolymerized rubber hydrocarbon present in the chloroform extracts obtained by alkali digester reclaiming showed the phenomenon of recovery if stored under vacuum for only one week.

It is rather interesting to compare the chloroform extract values of the heater-process and the digester-process reclaims (Figure 9). The heater process and the alkali digester-process reclaims yield chloroform extracts which are very similar in amount and rate of increase. The same picture is observed for the metallic chloride and the water reclaims. A scrutiny of the unsaturation value curves observed for the four kinds of reclaim shows a similar trend.

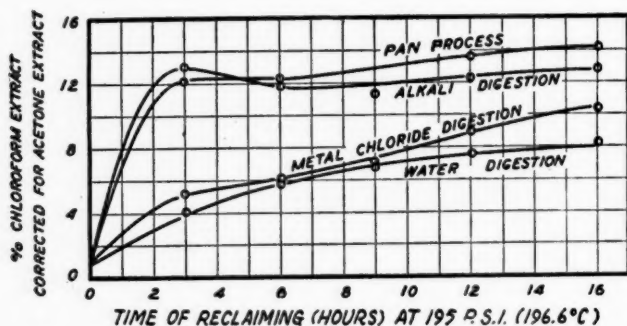


Fig. 9.—Comparison of chloroform extract values of reclaimed rubber produced by heater and digester processes.

EFFECT OF ANTIOXIDANT

A vulcanized compound identical with the one described before was prepared for this purpose, containing 1.5 parts of di- β -naphthyl-*p*-phenylenediamine. The scrap obtained from it was subjected to heater-process and also alkali digester-process reclaiming. Analysis of these reclaims for unsaturation yielded values which were almost identical with those obtained previously for the compound which did not contain any antioxidant.

Figure 10 shows that the increase in acetone extract during heater-process

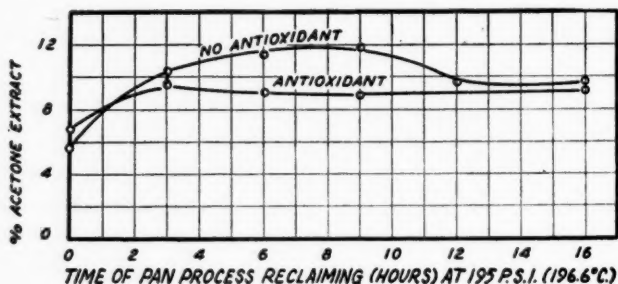


Fig. 10.—Effect of antioxidant on acetone extract values of pan- or heater-processed reclaimed rubber.

reclaiming is less for the compound containing the antioxidant, and that the acetone extract remains practically constant over the periods of time investigated. At the same time the formation of chloroform extract proceeds at a slower rate, and does not reach the same values as those of the compound which did not contain antioxidant (Figure 11). Both curves are identical in

their trends, and even in the presence of antioxidant the greatest rate of chloroform extract formation is obtained during the initial reclaiming periods.

No such effect can be noticed for the acetone extract values of the alkali-treated reclaim. The values obtained for the acetone extract of the alkali reclaim containing the antioxidant (Figure 12) are at all times about 1.5 per

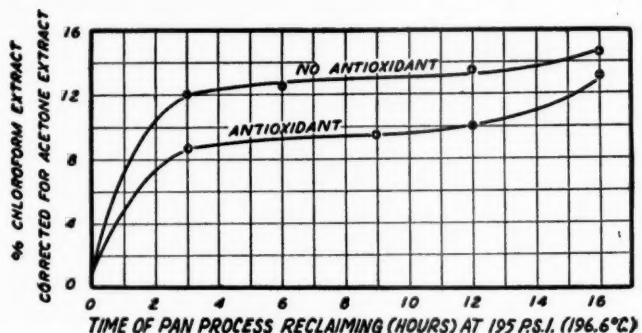


Fig. 11.—Effect of antioxidant on chloroform extract values of pan- or heater-processed reclaimed rubber.

cent higher than those obtained from the alkali reclaim which did not contain antioxidant. This amount and its constancy over all the periods of reclaiming investigated led to the assumption that the difference between these two acetone extract curves is due only to the presence of the acetone-soluble antioxidant. Apparently no more or less oxidation occurs during alkali reclaiming whether or not the antioxidant is present. A comparison of the chloroform extracts, however, shows that the addition of antioxidant decreases both its

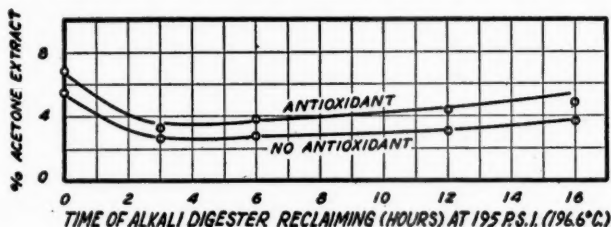


Fig. 12.—Effect of antioxidant on acetone extract values of alkali digester-processed reclaimed rubber.

amount and rate of formation (Figure 13). The change in rate of formation and in the magnitude of both the acetone and chloroform extracts of these reclaims indicates the part which oxygen availability plays in the reclaiming of natural rubber scrap.

DISCUSSION OF RESULTS

In discussing the results obtained from the experiments reported in this paper, it is desirable to review our present knowledge with regard to the molecular breakdown of rubber. It is well established by now that mill breakdown of natural rubber depends on the presence of at least minute quantities of oxygen⁷. Thorough investigations have shown that actual molecular oxidation

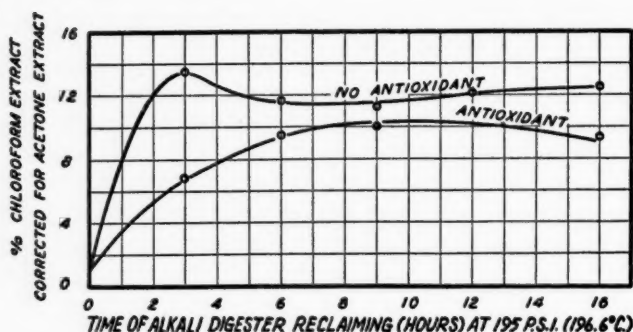


Fig. 13.—Effect of antioxidant on chloroform extract values of alkali digester-processed reclaimed rubber.

of the rubber hydrocarbon molecules, coupled with loss in unsaturation, does not occur except in extreme cases of overmilling. The formation of peroxides during the milling process has been proved⁸.

Hydroperoxidic oxidation reactions following a chain mechanism have been encountered in olefins and followed experimentally. Their reaction possibilities have been thoroughly discussed⁹ with special reference to such long-chain olefins as natural rubber. It has been shown also that temperature by itself need not affect crude natural rubber provided even traces of oxygen are excluded. Under such conditions rubber can be heated to 200° C for several hours¹⁰ without apparent molecular breakdown.

Vulcanized natural rubber is equally affected by oxygen. It can be reclaimed at elevated temperatures by milling, again provided that minute quantities of oxygen are present¹¹. Furthermore it is well known that the introduction of oxygen or oxygen-releasing chemicals into the digester vessel speeds up the reclaiming reaction. But it is equally well known that the presence of greater quantities of oxygen during this process exerts an adverse effect and produces a reclaim of inferior properties. Reclaim prepared from natural rubber scrap and from unvulcanized natural rubber both show the phenomenon of recovery during the period of storage following the reclaiming and the milling processes⁵. The recovery of the reclaim is shown by the decrease of the chloroform extract and the change in milling properties of the reclaim with time of storage.

Detailed experiments carried out over a number of years have shifted the old concept of primary molecular oxidative attack on the rubber toward one of hydroperoxidative attack¹². Olefin hydroperoxides are highly unstable compounds; however, they are still evident in milled rubber which has been stored for one week³. The formation of active radicals is now considered the first step in the hydroperoxidation of olefinic systems. A certain amount of energy—which can be supplied thermally—is required for the formation of these radicals⁹. A certain amount of oxygen attack occurring additively on the double bond and initiating the subsequent chain reaction has also been considered possible for the course of the overall reaction⁹. Such attack need occur only to an insignificant degree and, consequently, would cause only very small changes in unsaturation.

There is no doubt that the conditions under which reclaiming is carried out permit the supply of energy and also oxidative attack on a small scale. The

data presented above show that the unsaturation of the rubber hydrocarbon did not decrease to any significant extent; hence the main reaction occurring during reclaiming cannot be attributed to outright addition of oxygen on the double bond. At the same time, however, the chloroform extract, denoting chain scission, increased with time of treatment. Energy calculations and resonance considerations indicate that the rubber chains are most likely broken at the so-called isoprene link single C—C bond. Thus, unless actual oxidation proceeds very far, a decrease in the unsaturation of the chloroform extract of the reclaim should not be expected and actually was not found to occur.

It would be of great interest to study the reclaiming processes in the presence of accurately controlled amounts of oxygen. Unfortunately, however, this study is practically impossible. The ground vulcanized scrap exposes a tremendous surface during reclaiming. Experiments carried out at elevated temperatures and concerned with the decay of stress in vulcanized rubber have shown that even traces of oxygen present in the surrounding atmosphere influence the results to a considerable degree¹³.

The possibility of the formation of hydroperoxides during the grinding of vulcanized scrap before reclamation cannot be ignored. Furthermore the scrap may itself be partly oxidized before reclaiming.

Steam or water, or the solutions of the defibering agents in water, all of which constitute the surrounding atmospheres during reclamation, contains a certain amount of oxygen. Fresh steam is introduced during heater process reclaiming whenever it is necessary to maintain the pressure, thereby changing the amount of oxygen available at any given time. The double-jacketed digester, of course, at all times contains some air.

Even if an accurate study of the amounts of oxygen necessary for reclamation is not possible, all information available so far indicates the necessity of the presence of oxygen during reclamation, and stresses the fact that only small amounts of it accomplish the goal. Therefore outright oxidation of the natural rubber hydrocarbon can be discarded as basis for the reclaiming reactions, and it is necessary to focus attention on reactions which may occur in the presence of very small amounts of oxygen.

Two possibilities can immediately be visualized: a permanent introduction of oxygen into the rubber molecules by chemical valency forces or a peroxidative breakdown of the molecules similar to that which occurs during the milling of natural rubber. In the first case we might expect an increase in the acetone extract and a decrease in the unsaturation of the reclaim. In the case of peroxidative breakdown of the rubber, very little, if any change in the amount of unsaturation of the reclaim should occur unless fragments resulting from the chain reaction mechanism react with each other. This condition could be expected to occur at the longer reclaiming intervals. In the first case the further assumption would have to be made that only very few oxygen bonds would be necessary to replasticize the scrap. There is no justification for such an assumption, however, since even if actual molecular oxygen combination should occur, replasticization of the rubber can be expected only if it is accompanied by molecular breakdown.

The increase in the chloroform extract of the reclaimed rubber undoubtedly indicates the occurrence of molecular breakdown, but high chloroform-extract unsaturation values preclude the occurrence of secondary oxidative attack at the double bond. On the other hand, the increase in the acetone extract of the reclaim indicates serious oxidative attack on the hydrocarbon molecules, and

the very nature of the heater process undoubtedly provides a good medium for such attack. It is interesting to note the very high rate of molecular chain breakdown which occurs during the early stages of heater process reclaiming. This may be related to a peroxidative chain reaction mechanism, where after the comparatively short time interval necessary for the initial formation of radicals, a high rate of activity can be expected, owing to the nature of the reaction. These peroxides are thermally unstable, and as the time of reclaiming increases a great number of active radicals is formed, the presence of which may lead to reactions between themselves, resulting in mutual inactivation, thereby decreasing the overall reaction possibilities. At the same time actual oxidative attack at the double bond becomes noticeable. As will be shown later, a high rate of molecular chain breakdown during the early stages of reclaiming need not be connected with the formation of a considerable amount of actually oxidized material.

The rate of oxidation and molecular chain breakdown of the water digester reclaim is very much smaller than that of heater-process reclaim. This point is not surprising if it is remembered that the former was fully submerged in water during the entire reclaiming period, offering less change for oxygen to react with the rubber hydrocarbon. It is a well known fact that the production of heater-process reclaim requires shorter reclaiming intervals at a given temperature than the production of water digester-process reclaims.

The great differences in the results of the experiments observed for the two different groups of defibering agents can be explained on the basis of the differences encountered for peroxidative chain reactions in alkaline or acid media. In acid media the decomposition of olefin peroxides was found to go largely along the lines of Triol formation, which would not call for any loss in unsaturation⁹. The metallic chloride solution provides an acid medium during the reclaiming process, and no loss in unsaturation was found for reclaims prepared in the presence of metallic chlorides. Also water digester treatment results in a slightly acid medium. Thus the identical trend and the practical coincidence of the results obtained for acetone and chloroform extract, as well as for the unsaturation of these two kinds of reclaim, find its explanation.

The decomposition of the olefinic hydroperoxides proceeds much further and at a greater rate in an alkaline medium than in an acid medium. Also reactions between olefins and olefin peroxides are favored thermally. Such reactions would cause a decrease in the unsaturation⁹. A decrease in unsaturation was actually observed in the case of the alkali reclaim. The postulated increase in the rate of the peroxidic reaction can be seen in the enormous rate of molecular chain breakdown occurring during the initial periods of alkali-process reclaiming, compared to that obtained by reclaiming in a metallic chloride or water medium. Later on, possibly owing to the reactions between olefin and olefin peroxides the amount of molecular-chain breakdown does not increase any further, but the unsaturation of the reclaim decreases. Such reaction products between olefins and olefin peroxides may again become insoluble in chloroform. It can, therefore, be expected that while the amount of chloroform extract practically does not increase and its unsaturation remains high, during prolonged reclaiming periods, the unsaturation of the total reclaim should decrease owing to the presence of the olefin-olefin peroxide reaction products.

The presence of antioxidant causes a decrease in the rate of the molecular-chain breakdown during alkali digester reclaiming (Figure 13). At the same time, however, the conclusion might be drawn that the presence of alkali does

not enhance outright secondary oxidation. The two acetone extract curves (Figure 12) run absolutely parallel and differ only in their amount; the difference is of such magnitude as can be accounted for by the amount (1.5 per cent) of antioxidant added to the original compound. (This is distinctly in contrast to the results obtained from the reclaims produced by the heater process, where the presence of secondary oxidation reactions is influenced by the antioxidant, and these cannot be dismissed, even if chain breakdown may also be predominant.)

Thus the great practical differences between heater, alkali, and metallic-chloride digester-process reclaims which the reclaimer recognized a long time ago, have found their counterpart in the different reactions occurring during these reclaiming processes. Reclaiming oils—depending on their chemical nature—may or may not enter into the reactions. Depending on the process utilized during reclaiming, both secondary oxidation as well as hydroperoxidic breakdown of the hydrocarbon molecules can be expected to occur. However the presence of secondary oxidation reactions attacking at the double bond is by no means a necessary prerequisite for the reclaiming process. On the contrary, the occurrence of such reactions to any considerable degree is not desirable. The kind of surrounding atmosphere during the reclaiming process must be considered the determining factor for the reclaiming reaction mechanism and also to a large extent for the properties of the finished reclaim.

It might be expected that the actual detection of hydroperoxidic groups in reclaim would be difficult. These groups are thermally very unstable, and a chemical analysis is complicated by the presence of the compounding ingredients. The formation of active reaction centers is much greater during short reclaiming periods. Therefore it can be expected that those reclaims which were subjected to short reclaiming intervals should be highly unstable during prolonged storage, and show continued molecular breakdown, provided that hydroperoxidic chain reactions occur during the reclaiming processes.

From the data that was obtained so far it would also be expected that in this case the alkali digester reclaim would be the least stable reclaim during storage, followed by the heater-process reclaim, whereas water and metallic-chloride digester-process reclaims would be more stable. Investigations along that line are being carried out. Infrared spectrograms of the reclaims will provide information with regard to the presence of $C=O$ and OH groups in the reclaims.

One consideration in connection with the reclaiming of GR-S should finally be mentioned. The point for hydroperoxidation has been found to be connected closely with the substituent group attached to the carbon atoms connected by the double bond. The methyl group present in the isoprene unit of natural rubber enhances hydroperoxidation at the α -methylenic carbon atom. GR-S does not contain any substitutional groups on the carbon atoms at the double bond; therefore we may expect that the hydroperoxidic reactions proceed at a different rate from those in natural rubber. This, among other structural differences between the two polymers, undoubtedly also contributes to the difficulties encountered in the simultaneous reclamation of natural rubber and GR-S scraps.

SUMMARY AND CONCLUSIONS

The influence of surrounding atmosphere, antioxidant, and defibering agents at 196.6° C on the hydrocarbon of rubber was studied by subjecting a laboratory prepared, pure-gum, natural rubber compound to reclaiming in the absence of any reclaiming oils or chemicals.

Data obtained on the amount of acetone and chloroform extracts and on the unsaturation of the reclaims and the chloroform extracts could therefore be interpreted in terms of the effect of the factors mentioned above on the rubber hydrocarbon and not as the effect of any chemicals added to the rubber to promote reclaiming.

It was found that the effect of the surrounding atmosphere during reclaiming is the predominant factor in the reaction.

Acidic surrounding atmospheres result in a slow and rather uniform rate of molecular breakdown and in the formation of small amounts of oxidation products. Apparently no secondary oxidative attack occurs at the double bonds.

An open steam atmosphere provides the greatest amount of oxidized products and also a high initial molecular breakdown, followed by a slow progressive increase in it as the reclaiming periods are lengthened. A decrease in the unsaturation value of the acetone extracted reclaim indicates that secondary oxidative attack at the double bonds occurs at long reclaiming intervals.

Alkaline reclaiming atmospheres provide little if any oxidation products and result in a very high initial rate of molecular breakdown. Longer reclaiming periods do not change further the amount of molecular breakdown.

The very small amounts of oxygen necessary to promote the reclaiming reactions, the dependence of the course of these reactions on the acidity or alkalinity of the surrounding reclaiming media, together with the high initial rate of molecular breakdown reactions under conditions where such rate would be speeded up, permit the tentative explanation of these reactions on the basis of hydroperoxidic chain reactions. Further experiments along this line are being carried out.

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QUANTITATIVE ESTIMATION OF GR-S IN RUBBER RECLAIM*

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The identification of GR-S and its estimation in scrap rubber and reclaimed rubber have been the object of considerable research during recent years. Although it has become economically and practically impossible to segregate synthetic and natural rubber scrap, it still is of interest to determine the proportion of GR-S in the finished reclaim for the purpose of evaluating its properties.

Accurate methods have been worked out for the quantitative determination of GR-S in mixtures with natural rubber, but they require either a considerable amount of time or the use of expensive apparatus not accessible to the average reclaim manufacturer. Several of these methods can be carried out only after the hydrocarbon polymers have been brought into solution, and this, as far as reclaim is concerned, introduces difficulties. The average reclaim manufacturer or compounder is, in general, not concerned with a highly accurate estimation of GR-S in reclaim mixtures, but prefers a method which is fairly easy to carry out, and makes it possible to estimate GR-S within 5 parts of the total hydrocarbon present.

RUBBER HYDROCARBON CONTENT

For some time the evaluation of reclaim has been based on either the direct or indirect determination of its rubber hydrocarbon content. The direct determination is carried out by chromic acid oxidation¹, which gives the quantity of natural rubber hydrocarbon; the indirect, or difference method, by complete analysis of the sample and deducting the sum total of the acetone extract, ash, carbon black content, etc., from 100. The difference is considered to be the total rubber hydrocarbon content, which includes that of both natural rubber and GR-S.

Inasmuch as the presence of the methyl group in the position it occupies in the isoprene unit is mandatory as far as the chromic acid oxidation method is concerned, it is not surprising that butadiene-styrene copolymers does not yield acetic acid by this method. Repeated analysis of GR-S yielded only at the most 3 to 4 per cent of rubber hydrocarbon, and values of 1 to 2 per cent were found more generally. Reclaiming of vulcanized GR-S would not be expected to change this condition. Experiments have confirmed this point of view.

It was felt, therefore, that if the percentage of rubber hydrocarbon for any given sample by the above analysis were a direct function of either of the two kinds of polymers present, the proportions of each could be estimated by means of a simple plot based on the two rubber hydrocarbon contents, one obtained

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by difference and one by direct analysis. Inasmuch as GR-S practically does not take part in the formation of acetic acid by chromic acid oxidation, the value obtained for the rubber hydrocarbon content by difference should represent the sum total of the two polymers present, whereas the rubber hydrocarbon obtained by direct analysis should be a function of the content of natural rubber. Thus the values obtained by direct analysis of various mixtures containing GR-S would fall on a straight line proportional to the percentage of GR-S and natural rubber in these mixtures.

For this purpose GR-S and natural rubber reclaims were prepared separately, and carefully and completely analyzed. Seven predetermined mixtures of these reclaims were then prepared with analytical accuracy to cover the whole range from 100 per cent GR-S to 100 per cent natural rubber. The percentages of rubber hydrocarbon by direct analysis of these mixtures were determined. Figure 1 (dashed line) shows the data obtained for such a series plotted against the known proportions of GR-S and natural rubber for each mixture. Except for mixtures very high in GR-S, a straight line was obtained. The aberration

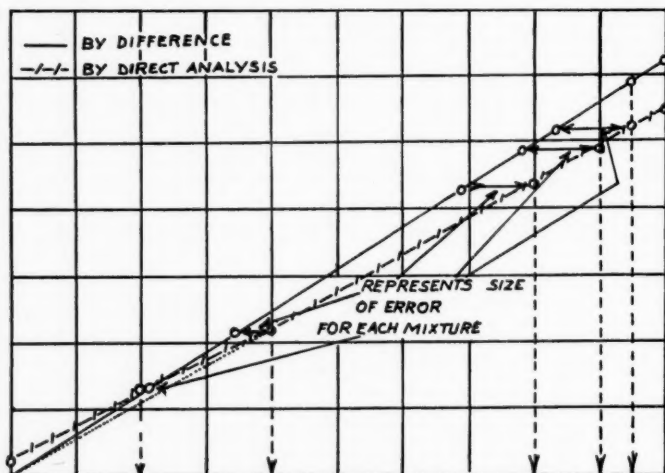


Fig. 1.—Rubber hydrocarbon in mixtures.

at high GR-S contents is a consequence of the slight amount of rubber hydrocarbon obtained for GR-S. This effect is bound to cause an error in the estimation of reclaims containing 90 per cent or more GR-S. Practically, however, the straight line can be extrapolated to the zero point without changing the results to any greater extent in mixtures less rich in GR-S.

To apply this method to industrial use, the estimation of a mixture of natural and synthetic rubber of unknown proportions would have to be based also on the percentage of total rubber hydrocarbon as determined by the difference method, because this latter value represents the sum of both natural and synthetic rubber hydrocarbon. In the case represented by Figure 1, this value was found to be 62.9 per cent. As such it can be considered and recorded on the graph as 100 parts of polymer. This value must be the end point of the straight line originating at the zero point. The data obtained from the various mixtures analyzed were replotted on this basis, and are shown in Figure 1 (solid line). If the data found by direct rubber hydrocarbon analysis are

plotted on that line, the parts of GR-S and natural rubber reclaim which can be derived from the abscissa of this plot do not correspond to the actual analytical mixtures prepared. A mixture actually containing 100 per cent of natural rubber reclaim seems to contain 88.5 per cent; 95 per cent natural rubber reclaim, only 83.5 per cent; 80 per cent natural rubber reclaim, 69 per cent; 40 per cent natural rubber reclaim, 34.5 per cent; 20 per cent natural rubber reclaim, 21.5 per cent; and no natural rubber, 3 per cent. The greatest error in estimation occurs for mixtures high in natural rubber. The less the proportion of natural rubber, the smaller the error appears to be. However, the error introduced in this way was found to be so great that until the reason for it and correction factor could be found, the method could not be considered useful.

The rubber reclaiming industry has known for some time that the values obtained for the rubber hydrocarbon content of natural rubber reclaim by direct analysis are in almost all cases lower than those obtained for the same reclaims by the difference method. This difference is referred to below as the deviation.

DEVIATIONS

It has often been assumed that the deviation between the two values of the natural-rubber hydrocarbon determinations is due to analytical errors and as such must be considered entirely accidental. However, if this were true, the rubber hydrocarbon content obtained by direct analysis would not always be lower in value than that obtained by difference. The sum total of errors introduced in the latter case would be cumulative, owing to errors obtained in each single analysis of the various ingredients in the reclaim. Analytical errors, however, like any other errors, can be positive as well as negative. Thus, even if analytical errors were the sole cause of the deviation between the two rubber hydrocarbon determination methods, they should not cause the rubber hydrocarbon determination by difference to be constantly of higher value than that obtained by direct analysis.

The yield of acetic acid obtained by chromic acid oxidation is expressed in fractions of gram-moles of acetic acid per gram-mole of methyl groups present. For natural rubber the yield amounts to 0.75, which indicates that 4 isoprene units form 3 moles of acetic acid. Combined sulfur can be expected to interfere with this reaction, necessitating the introduction of a correction factor. Results obtained by the oxidation of hard rubber² have indicated that, with about 3 atoms of combined sulfur, 2 isoprene units fail to yield acetic acid; in other words, for every 3 atoms of combined sulfur, 1.5 moles of acetic acid are lost.

Inasmuch as combined sulfur is not removed during the reclaiming procedure, part of the rubber hydrocarbon in reclaim is not available for further vulcanization. It is only logical to assume that this is the same part of the rubber hydrocarbon that does not enter into the chromic acid oxidation.

Thus the deviation between the two determinations of rubber hydrocarbon might be explained by the fact that a small amount of unsaturation is lost during vulcanization of the original crude rubber, and that some unsaturation may also be lost through oxidation, both of which would be expected to disturb the quantitative chromic acid oxidation to acetic acid. The factor of oxidation cannot be discounted. Burger² found the deviation much greater for reclaims than for vulcanizates not containing reclaim. Experiments on a natural rubber gum stock, which did not contain antioxidant, showed considerable

deviation when this stock was subjected to exaggerated reclaiming conditions which permitted considerable oxidation. The original vulcanized compound yielded 86 per cent of natural rubber hydrocarbon as determined by direct analysis, but when subjected to the highly oxidizing reclaiming conditions yielded only 76 per cent of natural rubber hydrocarbon. Naturally, such exaggerated conditions do not exist with actual reclaiming procedures. The scrap subjected to reclaiming contains antioxidant and in most cases carbon black, both of which permit a certain amount of protection against oxidation. The conditions under which reclaiming is carried out usually do not permit any sizable amount of oxidation; therefore such large deviations as mentioned above cannot be expected to occur.

Inasmuch, however, as a deviation occurs at all times in natural rubber reclaim, it also plays a part in any estimation of the GR-S or natural rubber present in mixtures such as those analyzed above. If this is true, the greater the deviation between the rubber hydrocarbon content by difference and by direct analysis of the natural rubber reclaim present the larger the error in the estimation of the components of the mixtures. This deviation was considerable for the natural rubber reclaim used in Figure 1. Furthermore, the error in the estimate of the components of the mixtures is much greater if these mixtures contain considerable amounts of natural rubber. Figure 1 shows that the error in estimation decreases gradually as the proportion of GR-S present in the mixture increases.

Therefore, it was decided to examine this deviation for natural rubber reclaims, such as peels, carcass, tire, and tube reclaims, in greater detail. Ample data for such critical scrutinization are available in any control laboratory of the rubber reclaiming industry. These laboratories have carried out complete analyses of natural rubber reclaims for product control and sales purposes over a number of years.

For this purpose the various natural rubber reclaims were grouped together according to the origin of the scrap from which they had been prepared. The same kind of graphic representation was used; the value of the rubber hydrocarbon content was assigned by difference on the ordinate of the system to a value equivalent to 100 parts of natural rubber reclaim on the abscissa. Inasmuch as the value of the rubber hydrocarbon by difference represented at all times the total amount of polymers present, it could be considered as 100 parts of natural rubber. A straight line was then drawn through the origin, assigning a zero rubber hydrocarbon content to a zero content of natural rubber reclaim.

In this way each natural rubber reclaim was represented by a line, the slope of which was determined by its natural rubber hydrocarbon content by difference. On each line the value for the rubber hydrocarbon obtained by direct analysis for the particular reclaim was recorded. The fact that in each case the parts of rubber which could be read in this way on the abscissa were less than 100 indicated that the rubber hydrocarbon content obtained by direct analysis was less than that obtained by difference analysis. A great number of natural rubber reclaims were plotted in this way.

If this graphic representation is carried out separately for the reclaims originating from different kinds of scrap rubber, each kind of reclaim seems to possess a particular and characteristic range of deviation. For example, three natural rubber peel reclaims showed a range of deviation between 1.2 and 3 per cent of natural rubber; three black carcass reclaims, one between 6.0 and 8.0 per cent; three light-colored carcass reclaims, one between 10 and

12.5 per cent; and out of the twelve first, second, and third line natural rubber tire reclaims, nine showed a range of deviation between 3.4 and 7 per cent. The range of deviation is characteristic for each kind of reclaim and seems to be a function of the origin of the reclaim more than of the reclaiming formulas used for the reclaiming process. This behavior of the reclaims is generally true, but it fails in the case of certain specific compounding ingredients which interfere with the direct rubber hydrocarbon analysis. The difference in the deviation between carcass and peel reclaims cannot be ascribed to errors in analysis arising from the presence of cellulose or its decomposition products in the carcass reclaims. Reclaims prepared from cellulose-free scraps, such as tube reclaims and peel reclaims, also differ widely in their deviations; the tube reclaims exhibit much larger deviations than those encountered for peel reclaims.

Table I shows the average deviations of the three main groups of reclaims as found by actual analysis over a period of 2 to 4 years.

TABLE I
DEVIATIONS OF RECLAIMS

Reclaim	Average deviation found by analysis over 2-4 years	Mean deviation
Peel reclaim		
I	1.2	1.5
II	1.6	
III	1.6	
IV	2.9	
Carcass reclaim		
I	6.1	6.6
II	5.9	
III	6.9	
IV	7.2	
V	6.8	
First line whole tire reclaim		
I	4.2	3.8
II	3.7	
III	4.0	
IV	2.3	
V	3.8	
VI	3.6	
VII	2.7	
VIII	6.8	
IX	5.4	
X	3.3	
XI	3.7	
XII	3.0	
XIII	4.7	
XIV	5.0	
XV	2.1	

The mean deviation of tire reclaims falls between those of the peel and the carcass reclaims. This can hardly be called coincidence, but rather is to be expected. Tire reclaims must, after all, be basically considered as mixtures of peel and carcass reclaims. Reclaims prepared from highly reinforced compounds such as peel show the smallest deviation between the two hydrocarbon values, and reclaims which contain no carbon black as reinforcing agent, such as light-colored carcass reclaims, show the greatest. A tentative explanation of this phenomenon can be attempted in regard to the loss of acetic acid due to

vulcanization (loss of unsaturation) during the chromic acid oxidation. Furthermore, Thornhill and Smith³ found that the smallest loss in unsaturation occurred during the vulcanization of highly reinforced carbon black compounds, which age better than nonreinforced compounds. A drop in unsaturation ascribed to oxidation has been noted by several investigators during accelerated aging experiments.

The above seems to indicate that the deviation between the values of the rubber hydrocarbon by difference and by direct analysis cannot be regarded as entirely accidental or as due to cumulative errors occurring during analysis. On the contrary, a certain amount of statistical order is evident, indicating that these deviations are largely dependent on the compounds from which the reclaims have been prepared.

If the original data obtained by analysis are replotted, taking the deviation for the kind of reclaim used into consideration, it can be seen immediately that the magnitude of error, so predominant before this correction was applied, has become considerably smaller (Figure 2). Now a mixture known to contain

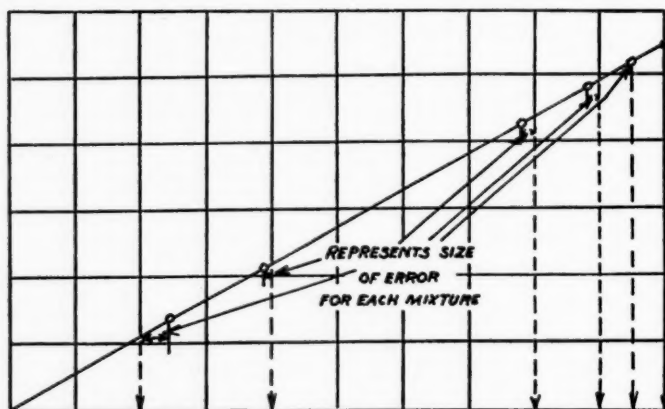


Fig. 2.—Rubber hydrocarbon in mixtures.

90 per cent of natural rubber seems to contain 88 per cent; 80 per cent of natural rubber, 78 per cent; 40 per cent of natural rubber, 39 per cent; and 20 per cent of natural rubber, 24.5 per cent. The higher the content of natural rubber, the smaller the error seems to be. The biggest error is encountered in mixtures rich in GR-S. However, the magnitude of the error has decreased to such an extent that the method becomes applicable for quantitative estimation of the components, at least for practical purposes. Correction for the deviation in proportion to the amount of natural rubber present in each mixture is automatically obtained by the slope of the line.

Algebraic calculation of the content of natural rubber or GR-S reclaim in their mixtures is equally possible. If no correction factor had to be taken into consideration, $S = T - R$, where S represented the percentage of GR-S, T the total rubber hydrocarbon content by difference, and R the percentage natural rubber. However, because of the slight amount of acetic acid obtained by chromic acid oxidation from GR-S, the experimental data obtained for R would be too high. Therefore, the actual value for the natural rubber present in the mixture can be expressed by $R_1 = R - aS$, where a is the amount of

acetic acid obtained from GR-S. Introducing this correction into the first equation, we obtain $S = \frac{T - R}{1 - a}$.

At the same time, however, the yield of acetic acid from vulcanized natural rubber and reclaim prepared from it has been found to depend on the amount of combined sulfur and to a certain extent on the oxidation of the rubber hydrocarbon. Therefore, another correction factor has to be introduced.

$S = \frac{T - bR}{1 - a}$ would then constitute the correct scientific formulation for calculation of the content of synthetic rubber reclaim in mixtures with natural rubber. The size of factor b would depend on the kind of scrap used (whole tires, tube, etc.).

Practically, however, factor a can in most cases be neglected. The limits of accuracy of the carbon black and cellulose analysis, both of which would enter into this formula by means of value T , are, in the case of reclaim, far from ideal. In determination of the direct rubber hydrocarbon content of reclaim, check analyses varying about 0.5 per cent are considered very good indeed. Thus, as the reclaim mixtures become richer in natural rubber the increment of acetic acid due to the presence of GR-S rapidly falls within the experimental limits of error, disqualifying the application of factor a . On the other hand, a mixture rich in GR-S does not justify the application of factor b . Practical experiments on such mixtures have shown that the smallest amount of error is actually obtained if factor b is not used. Actually, the estimation of GR-S reclaim would be much more accurate than ± 2.5 per cent if the limits of accuracy of the various analyses entering into the calculations were more favorable. Thus, it has been proved of practical expediency to use the correction for the deviation only in cases where direct analysis shows a comparatively large percentage of rubber hydrocarbon, indicating the presence of mixtures rich in natural rubber. Mixtures containing 15 per cent of less direct rubber hydrocarbon, or large amounts of GR-S, should be plotted without accounting for the deviation. Because only a small amount of natural rubber reclaim is present, the error due to the deviation between the rubber hydrocarbon content by difference and that by direct analysis is proportionately small and even compensates for the error due to the small amount of direct rubber hydrocarbon obtained from GR-S. Such mixtures are more accurately determined if no correction for the deviation is applied. Figure 3 shows the simplicity of the method.

PROCEDURE FOR ESTIMATING GR-S

Assuming that two unknown mixtures of tire reclaims have to be analyzed for their content of natural and synthetic polymer, the practical procedure for the estimation of GR-S would comprise the following steps:

1. Determination of the rubber hydrocarbon by difference.
2. Determination of the direct rubber hydrocarbon by chromic acid oxidation.
3. Ascertaining the kind of reclaim under consideration (tire, peel, carcass, tube, etc.).
4. Ascertaining the average deviation for this kind of reclaim.
5. Drawing the graphic plot. Plotting the percentage rubber hydrocarbon on the ordinate, the parts of natural rubber reclaim on the abscissa.

Assuming for the sake of illustration that one of the unknown mixtures gave:

1. A total rubber hydrocarbon content by difference of 60 per cent.
2. A direct natural rubber hydrocarbon content of 30 per cent.
3. First line tire reclaim.
4. Normal deviation for a natural rubber first line tire reclaim, 3.8.

5. The direct natural rubber hydrocarbon content of 30 per cent indicates a reclaim mixture fairly rich in natural rubber. Therefore the correction for the deviation should be applied ($60 - 3.8 = 56.2$): 56.2 per cent of rubber hydrocarbon constitutes the anchor point of the line going through the zero point of the graph. That line is followed down to an ordinate reading of 30 per cent natural rubber hydrocarbon, and the parts of GR-S reclaim are read at that point on the abscissa (see Figure 3).

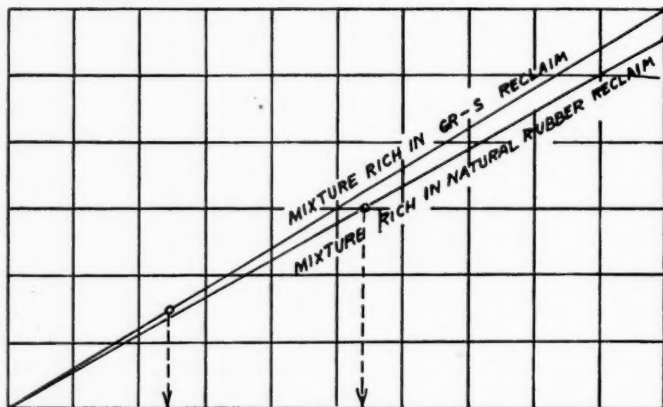


FIG. 3.—Rubber hydrocarbon in mixtures.

Assuming for the sake of illustration that the second of the unknown mixtures gave:

1. A rubber total hydrocarbon content by difference of 60 per cent.
2. A direct natural rubber hydrocarbon content of 15 per cent.
3. Not necessary.
4. Not necessary.
5. The direct natural rubber hydrocarbon content of 15 per cent indicates reclaim mixtures rich in GR-S. Therefore it is not necessary to apply any correction for the deviation. As 60 per cent rubber hydrocarbon constitutes the anchor point of the line going through the zero point on the graph, that line is followed down to an ordinate reading of 15 per cent hydrocarbon. The parts of GR-S reclaim are read at that point on the abscissa (see Figure 3). Figure 3, as well as these examples, must be considered a working example only.

First line tire reclaims show a smaller mean deviation than second or third line tire reclaims. Thus a much closer estimation can be made if it is known whether the reclaim in question is classified as first, second, or third line reclaim. If the method is used by a reclaim manufacturer to determine the GR-S content on one of the reclaims of his line, still greater accuracy can be obtained because the history of the production of this reclaim is probably known over a number

of years. In general, specific gravity and total rubber hydrocarbon content by difference will give the experienced worker some indications of the kind of reclaim with which he is working, and the correction for the deviation can thus be applied properly. The method should not be expected to be more accurate than ± 2.5 parts of polymer unless the origin of the reclaim and its behavior have been established. This is possible only if a reclaimer is trying to evaluate reclaim mixtures of his own production.

The originators of the rubber hydrocarbon determination by direct analysis have pointed out that certain substances, such as mineral rubber and greater amounts of cellulose, obscure this analysis and render it inaccurate. Consequently, the presence of such materials naturally also affect the estimation of GR-S or natural rubber unless they are removed before determining the rubber hydrocarbon content.

CONCLUSION

The method is none too accurate above 90 per cent of either natural or synthetic rubber present, unless the reclaim analyzed is well known. If the degree of deviation for a given reclaim is well established, it is possible to determine the mixtures up to 95 per cent of either component. However, if the degree of deviation is only an average figure, derived by such critical scrutinization of a number of reclaims as shown in Table I, greater accuracy cannot be expected in the estimation of the components of mixtures containing more than 90 per cent of either natural or synthetic rubber.

The GR-S or natural rubber content of reclaims containing a great variety of scraps, such as some of the so-called victory reclaims, can be estimated only with a lesser degree of accuracy than ± 2.5 parts. Difficulties in the estimation of the polymer components may also be encountered in light colored reclaims. However, such estimations are seldom necessary because of the peculiar compounding technique required by GR-S for proper physical performance.

ACKNOWLEDGMENT

The author wishes to express appreciation to N. Novakovich, who prepared the reclaim mixtures and carried out the analyses.

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HARDNESS TESTING OF VULCANIZED RUBBER.*

VII. INFLUENCE OF THICKNESS OF RUBBER.

TESTS WITH VARIOUS INDENTORS

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INTRODUCTION

In any form of hardness test which depends on the indentation of the rubber by a ball or plunger, the reading is influenced by the thickness of the rubber. Since excessive sensitiveness to thickness variations is undesirable, it was decided to investigate the cause of the difference in thickness-sensitivity between the various instruments.

Thus, some early published data suggested that the relative insensitiveness of certain instruments to thickness variations might be due to the use of a plunger of small cross-section.

Experiments were accordingly made with indentors of various types to find how sensitiveness to thickness variations can be reduced and also to examine other characteristics of those types of indentor that appear promising, *e.g.*, sensitiveness of the reading to variations in the hardness of the rubber at different parts of the scale, and sensitiveness to variations in period of application of the load, two points that must be taken into account in choosing the best type of indentor.

Some types of instrument have an indenting force that varies with the depth of the indentation, whereas others have a substantially constant force. The influence of this difference on sensitiveness to thickness variations has accordingly been examined.

EXPERIMENTAL

METHODS AND RESULTS

Most of the tests were made with the following two mixings:

	No. 1	No. 2
Smoked sheet rubber	95	95
Sulfur	5	5
Whiting	—	100
Stearic acid	—	2

Each mixing was press-vulcanized at 153° C (120 minutes for No. 1, 90 minutes for No. 2) in a mold the bottom surface of which rose in a series of steps, so that the thickness of the resulting slab of rubber increased in steps. By using this mold and a slow-vulcanizing mix, it was possible to obtain pieces of rubber of different thicknesses substantially alike in degree of vulcanization and therefore in true hardness.

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Hardness tests were made with the R.A.B.R.M. gauge¹, the period of application of the load being 30 seconds unless otherwise stated. Each measurement is the mean of at least four readings.

The following indentors were examined: $\frac{1}{4}$ -inch diameter ball, $\frac{1}{8}$ -inch diameter ball, $\frac{3}{32}$ -inch diameter ball for tests by the A.S.T.M. standard method²; 0.075-inch diameter ball (actually a plunger 0.075 inch diameter with a hemispherical end); plunger 0.075 inch diameter with flat end.

The results of the hardness tests are given in Table 1.

TABLE 1
DEPTH OF INDENTATION IN 100THS OF A MM.

Indentor load (g.)	$\frac{1}{4}$ -inch ball		$\frac{1}{8}$ -inch ball			$\frac{3}{32}$ -inch ball	0.075-inch ball	Plunger
	400	1000	500	630	1000	1360	370	500
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
<i>Rubber No. 1</i>								
12.3 mm. thick	90	166	146	169	243	373	156	161
6.4 mm. thick	83	145	137	157	220	338	148	151
3.9 mm. thick	73	120	125	139	189	280	135	135
2.7 mm. thick	65	98	110	124	159	215	120	117
1.6 mm. thick	54½	74	90	100	116	150	98½	88½
<i>Rubber No. 2</i>								
12.3 mm. thick	—	93	80	—	134	184	81½	67
6.4 mm. thick	—	86	75½	—	124	170	79	64
3.9 mm. thick	—	76	70	—	111	151	73	56½
2.7 mm. thick	—	65	62	—	94	129	67½	49
1.6 mm. thick	—	55½	55	—	81½	104	62	41½

INFLUENCE OF THICKNESS ON HARDNESS READING AND ON APPARENT HARDNESS MODULUS

Owing to the varying magnitude of the indentation, according to the type of indentor, load, and rubber, it is not easy from a casual inspection of Table 1 to see the relative extents to which thickness variations affect the readings in the various cases.

Moreover, these readings are not direct measurements of a physical property of the rubber, but merely arbitrary numbers connected in some way with the property termed hardness. True hardness may best be expressed as the hardness modulus³, which is proportional to the force required to produce an indentation of given depth with an indentor of given shape. This modulus is approximately proportional to Young's modulus measured at small extensions. The true hardness modulus is that measured on a piece of rubber of such thickness that the influence of the rigid supporting surface is negligible. On a thinner piece, such as is usually tested in practice, a greater force is necessary to produce the same indentation; the measured modulus is, therefore, higher than the true modulus, and may be termed the apparent modulus.

The effects of variation in the thickness of the rubber should therefore be regarded as changes in the apparent modulus, and the best hardness gauge is that in which a given variation in thickness has the least effect on the apparent modulus and so gives values nearest to the true modulus.

Table 2 gives values, calculated from the results in Table 1, for the difference in apparent hardness modulus between specimens 12.3 and 6.4 mm. thick, and between specimens 2.7 and 1.6 mm. thick; the difference is expressed as percentage of the mean for the two thicknesses (exact figures could not be ob-

TABLE 2
PERCENTAGE DIFFERENCE IN APPARENT MODULUS DUE TO
THICKNESS VARIATION

Indenter Load (g.)	$\frac{1}{4}$ -inch ball		$\frac{1}{8}$ -inch ball			0.075-inch ball	Plunger 500
	400	1000	500	630	1000	370	
	(a)	(b)	(c)	(d)	(e)	(g)	(h)
<i>Rubber No. 1</i>							
12.3/6.4 mm.	11	20	10½	12	12	6½	6
2.7/1.6 mm.	31	52	43	45	60	30	28
<i>Rubber No. 2</i>							
12.3/6.4 mm.	—	11½	8	—	10½	4	5
2.7/1.6 mm.	—	28	20	—	27	13	16½

tained for the $\frac{3}{32}$ -inch ball, owing to lack of the necessary auxiliary data for the calculation).

Table 2 indicates the following conclusions. (1) Increasing the load on a given ball increases the thickness effect. (2) The thickness effect is about the same on different rubbers if the thickness is the same and the loads are adjusted to give the same indentation—compare rubber No. 1 column (a) and No. 2 column (b). (3) Reducing the ball diameter without altering the load usually produces no improvement—compare columns (b) and (e). This would indicate that two opposing effects are at play: an increase in sensitiveness due to the increased indentation, and a decrease in sensitiveness due to the use of a smaller ball. (4) Reducing both ball size and load so as to keep the indentation about the same reduces the thickness effect—compare columns (c) and (g) with column (b). (5) There is no advantage in using a flat-ended plunger, since this gives practically the same results as a hemispherical ended plunger (ball) of the same diameter—compare columns (g) and (h). (6) The improvement due to reducing the ball size is relatively greater on the thick rubbers (12.3–6.4 mm. range) than on the thin ones (2.7–1.6 mm. range).

It can also be deduced from the data in Table 1 that the A.S.T.M. test, column (f), shows on the whole, no advantage over the $\frac{1}{4}$ -inch or $\frac{1}{8}$ -inch ball with 1000 grams; indeed, it is worse on the very thin samples. This is evidently because the advantage of the small ball is more than counterbalanced by the use of a heavy load which produces a very deep indentation (*cf.* Table 1).

DIRECT MEASUREMENT OF INFLUENCE OF THICKNESS ON APPARENT MODULUS

If the thickness of a piece of rubber is reduced, the indenting force must be increased by, say, x per cent to keep the indentation the same. The effect is the same as if the hardness modulus had been increased by x per cent without altering the thickness. By measuring the forces required to produce a given indentation on various thicknesses, the effect of thickness variation on the apparent modulus can thus be calculated directly. Table 3 gives results of tests of this kind. An additional test was made with the plunger, using an indentation of 135; this showed, as expected, that the thickness effect is increased when the indentation is deeper.

The columns in the lower part of Table 3 are lettered similarly to the corresponding columns in Table 2. Comparison of these Tables shows good agreement between the results obtained by the two methods. The results in Table 3 confirm conclusions (1), (4), (5) and (6) stated above in paragraph 2; there is no direct evidence bearing on conclusions (2) or (3).

TABLE 3

UPPER PART GIVES LOADS (GRAMS) REQUIRED TO PRODUCE THE INDENTATION STATED.
 LOWER PART GIVES THE DIFFERENCE BETWEEN LOADS FOR SUCCESSIVE
 THICKNESSES AS PERCENTAGES OF THEIR MEAN

Indenter Indentation mm./100	Rubber No. 1					Rubber No. 2 ¼-inch ball 55
	¼-inch ball	¼-inch ball	0.075-inch ball	Plunger		
	90	90	90	90	135	
12.3 mm. thick	391	267	182	290	424	315
6.4 mm. thick	475	295	195	308	455	335
3.9 mm. thick	600	348	217	345	512	367
2.7 mm. thick	780	423	250	390	608	441
1.6 mm. thick	1450	625	338	525	1090	532
	(b)	(c)	(g)	(h)		(c)
12.3/6.4 mm.	19	10	6½	6	7	6
6.4/3.9 mm.	23	16	11	11	12	9
3.9/2.7 mm.	26	19½	14	12	17	18
2.7/1.6 mm.	58	38	30	28	46	19

THEORETICAL CONSIDERATION OF THICKNESS EFFECT

The fact that the smaller the diameter of the indenter the less is the effect of variations in thickness, other things being equal, can be explained on theoretical grounds. It is convenient to consider the force required to produce an indentation as made up of two components: the indenting force (D) required for the local deformation involved in forming a hollow in the rubber surface, and the compressive force (C) required to compress the rubber between the indenter and the supporting surface; C is normally much smaller³ than D (see ref. 4). C should be approximately proportional to the area of contact between the indenter and the rubber (or more exactly the projection of this area on the plane of the rubber surface), other things being equal. For a shallow indentation of given depth produced by a ball, this area is proportional to the radius of the ball; for an indentation produced by a cylindrical plunger, or a deep indentation made by a ball, the area is proportional to the square of the radius. Hence, in general, C is proportional to R^n , where R is the radius and n is a constant between 1 and 2. It has been shown³ that D is proportional to $R^{0.65}$; hence C/D is proportional to $R^{n-0.65}$. Since n is always greater than 0.65, if R is increased C/D will increase; hence the fraction of the total force ($C + D$) which is required for compressing the rubber is increased. Since the degree of compression is a function of the thickness, increasing R thus increases the effect of thickness variations on the total force required to produce a given indentation, that is, on the apparent hardness modulus.

LOAD-INDENTATION RELATION FOR FLAT-ENDED PLUNGER

To convert the differences in indentation due to thickness variations into differences in apparent modulus, it was necessary to determine the relation between load and indentation for the flat-ended plunger. Experiments showed that provided the indentation was less than about half the thickness of the rubber, the indentation was substantially proportional to the load. It follows that with a given load the indentation should be inversely proportional to the apparent hardness modulus, or, if the thickness is constant, to the true modulus.

The latter conclusion can be confirmed from the results above (see Table 4). The modulus of each rubber can be deduced from the 1/4-inch ball indentation

by the formula previously given³; the modulus so obtained is very nearly inversely proportional to the indentation with the plunger, the product of the modulus and indentation varying by only 5 per cent over the range of rubbers Nos. 3 to 12 in Table 4.

TABLE 4
INDENTATION IN 100THS OF A MM.

Rubber†	Indentor Load (g.)	½-inch ball 1000	0.075-inch ball			Plunger 580
			403	460	425*	
No. 15. Thiokol plus gas black and fiber		19	17½	20	18½	—
No. 3. Magnesium carbonate tiling		20	17	20	18	8.7
No. 4. Black flooring		35	31	33½	32	—
No. 5. Silca soling mix (over)		61	56	62	58	44
No. 6. Tire tread		73½	69	78	72½	—
No. 7. Tire tread (under)		87	87	98	91	72
No. 8. Accelerated pure mix (over)		112	106	118	110½	100
No. 9. Accelerated pure mix (over)		137	134	149	140	—
No. 10. Accelerated pure mix		145	141½	156	147½	—
No. 11. Accelerated pure mix		153	148½	165	154½	160
No. 12. Accelerated pure mix (under)		163	160½	178	167	180
No. 13. Accelerated pure mix		182	186	213	196	—
No. 14. Rubber-sulfur (under)		207	227	260	240	257

* Calculated by interpolation from the 403- and 460-gram readings.

† Normally vulcanized except where indicated in brackets.

UNIFORMITY OF HARDNESS SCALE

An important point in comparing different types of indentor is the relative sensitiveness of the hardness reading to variations in modulus in different parts of the hardness scale. It would be advantageous to have an indentor such that a given small percentage change in modulus would produce the same difference in the reading (*i.e.*, the depth of indentation) irrespective of whether the rubber were hard or soft, that is, such that the sensitivity of the instrument to variations in hardness were substantially uniform.

With the three chief types of indentor (ball, flat-ended plunger, and cone) the relation between modulus (M) and indentation (H) under a given load is of the form: $H = kM^{-n}$ where k and n are constants. The values of n are: Ball, 0.74 (see Ref. 4); Plunger, 1.0 (see section above); Cone, 0.5 (this can be deduced by analogy with an equation of Scott⁴, and is confirmed experimentally by Scott⁵).

Consider two values of the modulus, one low (M_1) and one high (M_2). Let S_1 be the change in the indentation caused by a small percentage increase in M_1 , and S_2 the corresponding change caused by the same percentage increase in M_2 ; then S_1 and S_2 represent the sensitiveness of the instrument to small variations in modulus in the soft and hard regions, respectively. It is easily shown that: $S_1/S_2 = (M_2/M_1)^n$. Since M_2/M_1 is greater than 1, and n is always positive, S_1/S_2 is always greater than 1, *i.e.*, the sensitiveness is greater on the soft than on the hard rubber with all three types of indentor.

The difference in sensitiveness, however, must be greater the higher the value of n . The plunger thus shows in an exaggerated degree one of the defects of the ball, that is, relatively low sensitiveness on hard rubbers. On the other hand, the cone possesses this defect in a smaller degree than the ball. It is impossible to have an indentor giving uniform sensitiveness over the whole hardness scale, *i.e.*, such that $S^1 = S^2$, because this would necessitate n being

zero, which would mean that the indentation was independent of the hardness of the rubber.

CHOICE OF INDENTOR FOR HARDNESS GAUGES

The experiments described in paragraphs 1-3 above, show that, to render an indentation hardness gauge relatively insensitive to variations in the thickness of the rubber, the indenter must be of small cross-sectional area. It appears to be immaterial whether it has a flat or hemispherical end. It is necessary, however, to consider whether a small indenter possesses any disadvantages in other directions. In the relevant experiments described below, the $\frac{1}{4}$ -inch ball has not been included because it must be intermediate in behavior between the $\frac{1}{4}$ -inch ball and the very small indentors.

Relation of reading to that with "standard" ball

If a new size or type of indenter is to be introduced, it is desirable to be able, by suitably choosing the load, to make it give readings substantially identical with the test hitherto regarded as standard. To examine this point the readings given by the 0.075-inch ball and the plunger have been compared with those given by the $\frac{1}{4}$ -inch ball (which had been a widely accepted standard before these experiments), using a range of rubbers from the hardest to the softest normally met with. The results for rubber samples 10 mm. thick, are given in Table 4.

The flat-ended plunger gives readings lower than the $\frac{1}{4}$ -inch ball on the harder rubbers, but higher on the soft ones. As the indentation with the plunger is proportional to the load, altering the load could not make it give the same readings as the $\frac{1}{4}$ -inch ball over the whole hardness range.

The 0.075-inch ball, on the other hand, gives results closely proportional to those for the $\frac{1}{4}$ -inch ball up to readings of about 160, and by suitably choosing the load it can be made to give readings very close to those for the $\frac{1}{4}$ -inch ball (with 1000 grams) on all normal rubbers, as is shown by the figures for 425 grams. This close equality observed on 10 mm. thickness of rubber would not persist over the whole hardness range if thinner rubbers were used, because of the different extents to which the readings of the two balls are affected by thickness variations. This, however, is not a defect of the small ball, but rather of the large one, which is the more sensitive to such variations.

These experiments show that of the two types of indenter of 0.075-inch diameter, that with the hemispherical end (*i.e.*, the ball) is preferable to that with the flat end, as regards comparability of its readings with the old $\frac{1}{4}$ -inch ball standard.

The reason why the close relation between the readings of the 0.075-inch and $\frac{1}{4}$ -inch balls breaks down above a certain limit, about 160, is that when the indentation is deep a small indenter acquires the character of an elongated plunger rather than a ball, and therefore behaves more like the flat-ended plunger, giving higher readings than the $\frac{1}{4}$ -inch ball (see Table 4).

These and other experiments show that the indentation at which the close relation to the $\frac{1}{4}$ -inch ball breaks down is roughly proportional to the diameter of the small indenter, being about $\frac{2}{3}$ of the latter. There is, therefore, a lower limit to the reduction in the diameter of the indenter if correspondence with the $\frac{1}{4}$ -inch ball readings is to be maintained over the whole usual range of hardness.

Effect of period of application of load

Indentation increases gradually during the period for which the load acts⁶. Any considerable difference between two types of indenter as regards the magnitude of this increase would make the relation between their respective readings dependent on the period of loading. To investigate this point two rubbers in which the time effect is relatively large were chosen, namely, Nos. 7 and 14 (see Table 4). For comparison a well-vulcanized snappy rubber, No. 11, was tested to show the normal magnitude of this effect. Results are given in Table 5.

TABLE 5
INDENTATION IN 100THS OF A MM.

Rubber		No. 7		No. 14		No. 11	
Indenter (ball)	Load	$\frac{1}{4}$ -inch 1000	0.075-inch 403	$\frac{1}{4}$ -inch 1000	0.075-inch 403	$\frac{1}{4}$ -inch 1000	0.075-inch 403
Time in sec.:	5	83.1	83.0	197	214	151.5	147.4
	10	85.0	84.4	201	219	152.1	148.0
	20	86.7	86.5	204 $\frac{1}{2}$	224 $\frac{1}{2}$	152.7	148.7
	30	87.7	87.6	207	227	153.0	149.1
	45	88.7	88.8	209	230	153.4	149.4
	60	89.6	89.4	210	232	153.6	149.6
	90	90.6	90.5	212	234 $\frac{1}{2}$	153.9	149.8
	120	91.2	91.2	213 $\frac{1}{2}$	236	154.2	150.1
	300	—	—	217	241 $\frac{1}{2}$	—	—
	600	—	—	220	244 $\frac{1}{2}$	—	—

Only with the exceptionally plastic rubber No. 14 does the 0.075-inch ball show a distinctly different effect from the $\frac{1}{4}$ -inch ball. As, however, this rubber was chosen to show an exaggerated time effect, and as the difference over the normal loading period of 30 seconds is only 3 units, the 0.075-inch ball would not in normal usage be under a disadvantage as regards the influence of time on the hardness reading.

CONSTANT *versus* VARIABLE INDENTING FORCE

In some hardness-measuring instruments the force on the indenter is less the deeper the indentation, whereas with others it is substantially constant. It is, therefore, essential to know whether this feature affects the relative sensitivity of the two types of instrument to variations in the thickness of the rubber.

We may define the apparent hardness modulus of a piece of rubber (*A*) of ordinary thickness, say 1 cm., as being equal to the true modulus of another rubber (*B*) such that an infinitely thick piece of *B* gives the same indentation as the piece *A* under the same load. *B* must have a higher true modulus than *A*, and the difference between the true moduli of *B* and *A* represents the error in the measurement of the latter.

Since this comparison of moduli involves only indentations of one constant depth, it does not matter whether the indenting force varies with the depth of indentation or not, provided the force is the same in both cases at the depth in question. It follows that the effect of variations in the thickness of the rubber, expressed in terms of errors or variations in the apparent hardness modulus, is the same whether the load varies with the depth of indentation or not.

SUMMARY

To determine how the sensitiveness of hardness readings to variations in the thickness of the rubber depends on the form of the indenter and other factors, tests have been made with balls of $\frac{1}{4}$, $\frac{1}{8}$, and 0.075 inch diameter and with a flat-ended plunger of 0.075 inch diameter. The following conclusions are drawn. (1) The smaller the indenting ball, the less is the sensitiveness to thickness variations, provided the loads are adjusted to give about the same indentation with the different balls; this result is in accordance with the theory of hardness testing. (2) With a given ball size, any factor that increases the indentation increases the sensitiveness. (3) If the ball size is reduced without reducing the load, effects (1) and (2) approximately counterbalance, so no reduction of sensitiveness is obtained. (4) The flat-ended plunger shows no advantage over the round-ended plunger of the same diameter. (5) The A.S.T.M. hardness test ($\frac{3}{32}$ -inch ball with 3-lb. load) shows no advantage over the $\frac{1}{4}$ - or $\frac{1}{8}$ -inch ball with 1-kg. load, and would be less satisfactory than the more recent British Standard test using a $\frac{3}{32}$ -inch ball with a smaller load.

The 0.075-inch ball with 425-g. load gives practically the same readings on rubbers 1 cm. thick as the $\frac{1}{4}$ -inch ball with 1-kg. load over the whole normal range of hardness values, but if the ball size is further reduced, this close agreement does not extend over all of this range. The use of the 0.075-inch ball does not increase the variation of the hardness reading with period of application of the load.

With the flat-ended plunger, the indentation is approximately proportional to the load, and therefore inversely proportional to the hardness modulus of the rubber (provided the indentation is less than about half of the thickness of the rubber). Consequently, the plunger cannot be made to give readings identical with those of a ball indenter. Moreover, it exaggerates one defect of the ball type of indenter, i.e., lower sensitiveness to variations in hardness modulus on hard rubbers than on soft rubbers. On the other hand, a conical indenter reduces this defect.

To make an instrument that is relatively insensitive to variations in the thickness of the rubber and yet gives readings close to those of the earlier ball test ($\frac{1}{4}$ -inch ball with 1-kg. load), a ball nearer 0.075 inch diameter with a correspondingly reduced load should be used. (The method subsequently adopted as British Standard⁶, is the outcome of this recommendation.) On rubbers of the order of 1 cm. thick, the sensitiveness to thickness variations is thereby reduced to about one-third.

The use of spring loading (whereby the force on the indenter is less the deeper the indentation) instead of a constant load, does not affect the sensitiveness of the reading to thickness variations. The relative insensitiveness shown by the Shore and Cusson's Durometers, and the Rubbermeter, is due to their having small indentors, not to their using variable spring loading.

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VIII. HARDNESS TESTS WITH A CONICAL INDENTOR

J. R. SCOTT

INTRODUCTION

The conical indentor is of interest for the following reasons.

(1) With a ball indentor, the shape of the indentation varies with its depth, so it is difficult to deduce theoretically the relation between indenting force and depth of indentation; and indeed attempts to do so¹ have given results at variance with the relation found by experiment². With a cone, on the other hand, shape is independent of depth, so for a perfectly elastic material the required force should be proportional to the elastic modulus of the material and to the square of the depth of indentation.

(2) If the load/modulus/indentation relationship indicated above holds good, it follows that, when using a cone with constant force, the indentation should be inversely proportional to the square root of the modulus. The cone thus has the advantage that the modulus can be deduced approximately from the indentation by a simple relationship based on the theory of elasticity, whereas with a ball it is necessary to obtain an empirical relation from experiments.

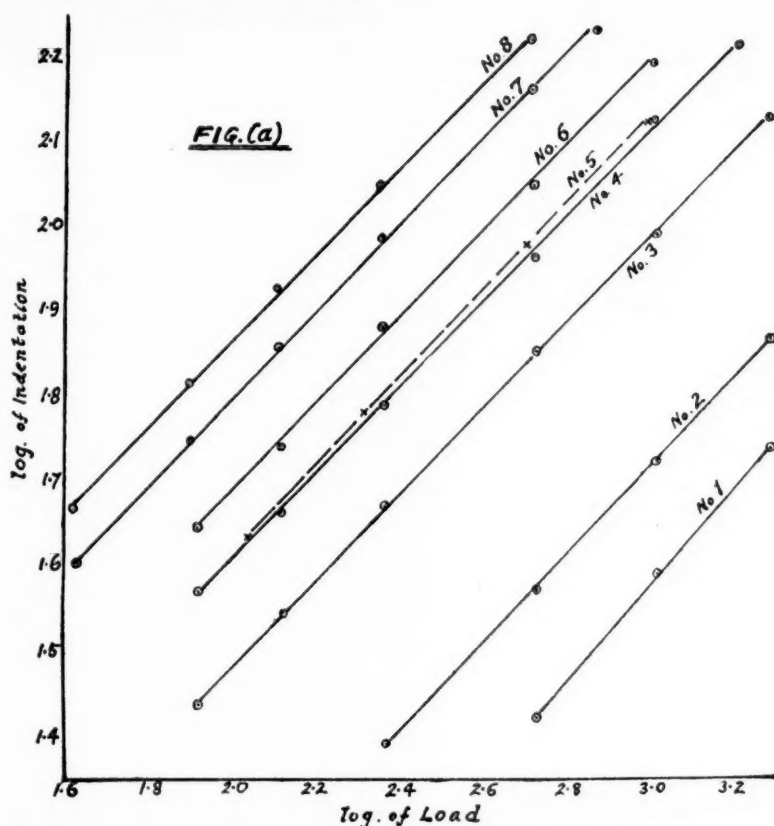
(3) The cone would be more sensitive on relatively hard rubbers than the ball indentor, as has already been pointed out³. This is an advantage, because the ball is comparatively insensitive in showing small hardness differences among hard samples.

EXPERIMENTAL

The indentor used was a steel cone of 120° angle having a radius of $\frac{1}{8}$ inch (3.2 mm.) at its base. The height of the cone was thus 1.8 mm., so in the hardness tests the depth of the indentation had to be kept less than this. Tests were made with an R.A.B.R.M. hardness gauge fitted with this indentor; the period of application of the load was 30 seconds, during which the supporting surface was gently tapped. Rubber samples about 10 mm. thick were used. The hardnesses measured with a $\frac{1}{8}$ -inch ball and 1-kg. load (*i.e.*, approximately British standard hardness numbers) are given below. Figure (a) shows indentation plotted against load, using logarithmic scales; the loads have been corrected for any lack of balance between the gauge springs and the weight of the loading platform, and so represent the true indenting force. Loads are expressed in grams, and indentations in mm./100.

Rubber:	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Hardness No.:	12	25	58	85	87	107	156	192

If the depth of indentation is proportional to the square root of the load, as theory indicates for perfectly elastic materials, the points for each rubber in Figure (a) should lie on a straight line, with a slope of 0.50. In every case the points do lie very nearly along a straight line, the slope of which has the following values: Rubber No. 1, 0.55; No. 2, 0.51; No. 3, 0.50; No. 4, 0.50; No. 5, 0.51; No. 6, 0.505; No. 7, 0.51; No. 8, 0.505. All these values agree well with the theoretical 0.50 except that for rubber No. 1, where the discrepancy is attributable to the fact that very hard rubbers such as this are not perfectly elastic. It may be concluded, therefore, that the theoretical relationship between



indenting force and depth of indentation by a cone holds good for vulcanized rubber, except that on rubbers rendered extremely hard and therefore inelastic by heavy compounding, there is some deviation from this relationship. It follows that, under a given load, the depth of indentation by a cone is, in general, inversely proportional to the square root of the modulus of the rubber.

The results also establish the greater sensitiveness of a cone (as compared with a ball) on relatively hard rubbers. Table 1 compares the readings given by a $\frac{1}{4}$ -inch ball with 1 kilogram and by the cone with 700 grams (this load has been chosen to make the readings on the softest sample about the same; the cone values are obtained from Figure (a) by interpolation or extrapolation).

TABLE 1
HARDNESS READING (DEPTH OF INDENTATION IN MM. 100)

Rubber	Ball	Cone
No. 1	11 $\frac{1}{2}$	31
No. 2	24	43 $\frac{1}{2}$
No. 3	58	81 $\frac{1}{2}$
No. 4	85	109
No. 5	87	113
No. 6	107	131
No. 7	156	169 $\frac{1}{2}$
No. 8	192	196

Among the harder samples, Nos. 1-4, the cone readings are more widely spaced out than the ball readings. Among the softer samples, they are less widely separated; however, this is not a disadvantage, because the ball is unduly sensitive on very soft rubbers by reason of its load/indentation relationship³.

SUMMARY

The relation between load and depth of indentation for a conical indenter has been investigated. The theoretical relationship applicable to perfectly elastic materials (indentation proportional to square root of load) is found to hold for all the rubbers examined except one very hard sample, whose comparative inelasticity causes some deviation from this relationship.

This result further confirms the correctness of the theoretical investigation on indentation hardness testing of rubber² by indicating that the forces required to produce indentations of similar shape, but different sizes, are proportional to the squares of corresponding linear dimensions of the indentations.

With a conical indenter under a constant load, the depth of indentation is approximately inversely proportional to the square root of the elastic modulus of the rubber at small elongations.

A conical indenter is preferable to a ball indenter in that it shows more nearly uniform sensitivity to small differences in modulus (*i.e.*, true hardness) at all parts of the hardness scale. It has previously been shown³ that the ball is superior to a flat-ended plunger in this respect. To approach still nearer to uniform sensitivity would presumably require a pointed indenter having a profile with concave sides. This would be difficult to make accurately, and very likely to damage on account of its sharp point; this might, indeed, be a disadvantage of the conical form also.

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IX. INFLUENCE OF THICKNESS OF RUBBER IN HARDNESS TESTING

J. R. SCOTT

INTRODUCTION

The result of any indentation hardness test is influenced by the thickness of the rubber, and this effect must persist at all finite thicknesses. The statement sometimes made that the hardness reading becomes independent of the thickness above a certain limiting thickness is only an approximation, though doubtless it is true enough for most practical purposes.

Unless the thickness is stated, the result of a hardness test is not fully defined. Since it is not always possible to carry out tests on samples of the same thickness, the value of hardness test results is considerably lessened if we cannot convert readings on one thickness into the corresponding readings on any other thickness. What is therefore needed for each type of hardness gauge is a conversion chart, *e.g.*, a set of curves of hardness number against thickness for

several rubbers of different hardnesses. It was mainly with the object of providing data for the construction of such charts that the present work was undertaken. Several rubbers of hardnesses ranging from very soft to very hard were prepared, each in several thicknesses, and each sample was tested with various hardness gauges, three different indentors being used with the R.A.B.R.M. gauge. From the results, information has been obtained on the sensitiveness of the different gauges to thickness variations, and also on the influence of indentor shape and dimensions on this sensitiveness, to supplement previous work on this aspect¹.

EXPERIMENTAL

The first series of rubbers examined had the following compositions:

	A	B	C	D	E	F	G	H	J
Smoked sheet rubber	100	100	100	100	100	100	100	100	100
Sulfur	3	3	3	3	3	3	3	3	2.5
MPC black	100	85	70	55	40	25	12	—	—
Zinc oxide	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1
Diphenylguanidine	1.25	1.25	1.25	1.25	1.0	1.0	0.75	0.75	0.5

All these mixings were vulcanized for 100 minutes at 141° C.

To determine whether similar relationships between thickness and hardness number hold for rubbers containing other fillers and (or) accelerators, or without accelerator, a second series of mixings was prepared, as follows:

	A2	B2	D2	E2	F2
Smoked sheet rubber	100	100	100	100	100
Sulfur	5.3	3	3	5.3	2.5
Barytes	—	—	120	—	—
MPC black*	—	65	—	—	—
Whiting	—	—	—	105	—
Zinc oxide	—	5	5	—	5
Stearic acid	—	1	2	2.1	1
Mineral oil	—	—	—	—	4
Diphenylguanidine	—	1.25	—	—	0.6
Hexamethylenetetramine	—	—	—	—	—
Methylene- <i>p</i> -toluidine	—	—	0.75	—	—
Vulcanization { ° C	153	141	141	153	141
minutes	120	100	100	90	100

* Different grade from that used in first series.

Specimens of different thicknesses, ranging up to 12.6 mm., were vulcanized by the procedure already described¹. In a few tests thicknesses greater than 12.6 mm. were obtained by superposing two pieces of rubber.

Tests were made with the R.A.B.R.M. gauge², Shore Durometer, Cussons Durometer³, and Rubbermeter⁴. With the R.A.B.R.M. gauge, the hardness reading was normally taken as the difference between the depths of indentation under a small zero load and under a much larger final load; the direct load quoted below is that which would give the same reading when used without a zero load. Tests with the R.A.B.R.M. gauge were made with 3 different indentors, as follows:

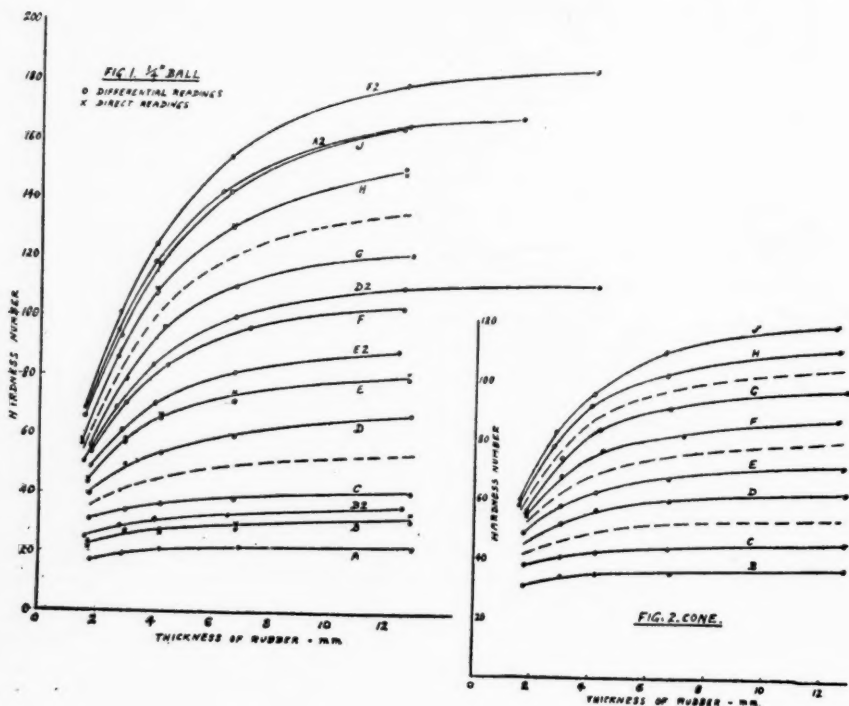
Indentor	Zero load	Final load	Equivalent direct load
Ball $\frac{1}{8}$ -inch diameter	23 g.	1083 g.	1000 g.
Ball 0.075 inch diameter	10 g.	470 g.	425 g.
Cone of 120° angle	23 g.	623 g.	410 g.

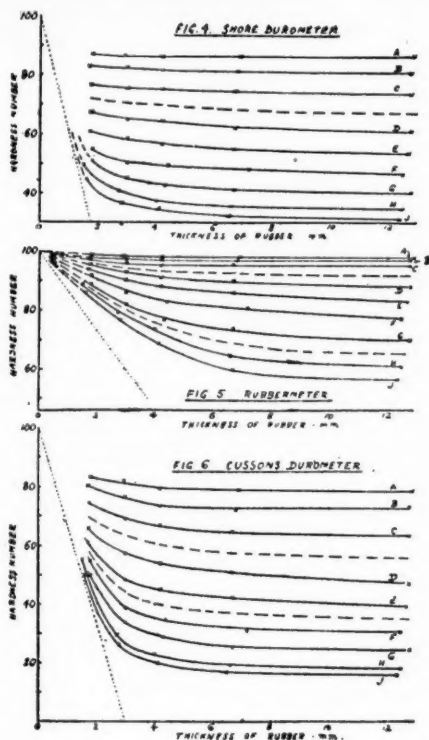
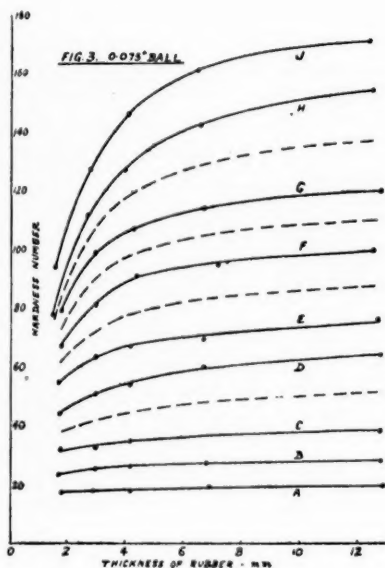
The loads used with the 0.075-inch ball are such as give about the same hardness reading as the $\frac{1}{4}$ -inch ball test on rubbers 1 cm. thick. The cone was the same as that used in previous work, which indicated certain advantages for this type of indenter⁵.

With the $\frac{1}{4}$ -inch ball a few tests were made with a direct 1000-gram load to check the correctness of the loads used in the differential method; Figure 1 shows satisfactory agreement between the direct and differential readings.

The results are shown in the form of curves of hardness number against thickness of rubber in Figures 1-6. In the tests with the R.A.B.R.M. gauge hardness number represents depth of indentation in mm./100; with the other gauges the hardness number is the arbitrary scale reading.

To facilitate the use of these graphs in converting hardness readings from one thickness to another, a few additional curves (broken lines) have been interpolated in the wider gaps between the experimental curves. The dotted line shown on each of Figures 4-6 is the theoretical thickness/hardness number curve for an infinitely soft rubber, *i.e.*, one having zero modulus. On such a rubber the indentation would equal the thickness of the rubber, and the thickness/indentation curve would be a straight line. This line represents the limiting member, in the direction of decreasing hardness, of the family of thickness/hardness number curves. The position of this line for the Shore Durometer shows that the curves for the softer rubbers must turn rapidly upwards below about 2 mm. thickness, as indicated by the extensions in broken lines.





DISCUSSION

CONVERSION OF HARDNESS READINGS FROM ONE THICKNESS TO ANOTHER

Figure 1 shows that the thickness/hardness number curves for rubbers containing different fillers and accelerators usually run parallel to one another. The parallelism, however, is not always exact (see *e.g.*, F2, A2, and J), so that a thickness conversion chart cannot be made strictly accurate for all rubbers. This is not surprising, since vulcanized rubbers are not perfectly elastic, but always show some degree of plasticity.

Using the curves given in Figures 1-6, it is a simple matter to convert hardness readings obtained on any thickness within the range examined (1.7-12.6 mm.) into the corresponding readings for any other thickness. If the original thickness and hardness number fall on one of the curves, it is necessary only to follow the curve to the new thickness and read off the hardness number corresponding to this point. If the original values correspond to a point lying between two curves it is easy for the eye to follow an imaginary curve passing through this point and running parallel to the adjacent curves, a proceeding sufficiently accurate for most purposes.

These experiments were made before the $\frac{3}{32}$ -inch ball was introduced as the British Standard test⁶, but as this is very near in size to the 0.075-inch ball, the curves for the latter would be applicable approximately to the $\frac{3}{32}$ -inch ball, as has in fact been found in subsequent tests. A thickness correction based on these curves has been published⁷.

CONVERSION OF HARDNESS READINGS FROM ONE
INSTRUMENT TO ANOTHER

Since the different instruments are affected to different extents by variations in the thickness of the rubber, a curve for converting the readings of one instrument into those of another is, in general, valid only for one thickness of rubber. The data graphed in Figures 1 to 6 can be used to construct such conversion curves for any thickness within the range examined.

THICKNESS-SENSITIVITY OF VARIOUS INSTRUMENTS AND INDENTORS

Figures 1 to 6 show that the effect of thickness variations on the hardness number is not of the same magnitude with the different instruments or indentors. It is not possible, however, merely by inspecting the curves to estimate the relative extents to which the measurements of hardness by the different tests are affected by thickness variations, because the hardness number is not the same thing as hardness properly so-called.

Following the procedure adopted in earlier work on the thickness effect¹, thickness-sensitivity may be defined as the percentage change in apparent hardness modulus produced by a given small change, namely 1 per cent in the thickness of the rubber. The smaller the thickness-sensitivity of a hardness test the better, other things being equal.

From the thickness/hardness number curves, together with the known relations between modulus and $\frac{1}{4}$ -inch ball reading⁶ and between the latter and the

TABLE 1

THICKNESS-SENSITIVITY (PERCENTAGE CHANGE IN APPARENT MODULUS PRODUCED BY
1 PER CENT CHANGE IN THICKNESS) AND MODULUS-SENSITIVITY (DIFFERENCE
IN HARDNESS NUMBER CORRESPONDING TO 1 PER CENT INCREASE IN MODULUS;
VALUES ARE POSITIVE UNLESS MARKED MINUS)

Rubber Hardness No.*	Test	Thickness	Thickness-sensitivity				Modulus-sensitivity			
			B 31	D 65	F 101	J 158	B 31	D 65	F 101	J 158
	$\frac{1}{4}$ -inch ball	2 mm.	0.40	0.83	1.25	1.45	-0.15	-0.21	-0.25	-0.34
		5 mm.	0.23	0.34	0.46	0.77	-0.19	-0.39	-0.56	-0.70
		10 mm.	0.16	0.18	0.20	0.29	-0.21	-0.48	-0.68	-1.0
	0.075-inch ball	2 mm.	0.21	0.36	0.56	0.88	-0.16	-0.30	-0.46	-0.63
		5 mm.	0.13	0.24	0.22	0.29	-0.20	-0.41	-0.70	-1.05
		10 mm.	0.08	0.10	0.08	0.09	-0.23	-0.47	-0.76	-1.25
	Cone	2 mm.	0.34	0.79	1.15	1.35	-0.14	-0.16	-0.22	-0.26
		5 mm.	0.13	0.31	0.52	0.79	-0.19	-0.26	-0.32	-0.39
		10 mm.	0.08	0.14	0.19	0.25	-0.21	-0.30	-0.42	-0.53
	Shore Durometer	2 mm.	0.12	0.27	0.49	0.70	0.13	0.18	0.21	0.22
		5 mm.	0.09	0.14	0.14	0.19	0.15	0.21	0.23	0.25
		10 mm.	0.03	0.05	0.05	0.06	0.15	0.23	0.24	0.26
	Cussons Durometer	2 mm.	0.58	0.84	1.55	2.6	0.14	0.20	0.22	0.17
		5 mm.	0.22	0.28	0.28	0.30	0.17	0.24	0.28	0.21
		10 mm.	0.06	0.17	0.06	0.07	0.20	0.26	0.28	0.18
	Rubbermeter	2 mm.	1.0	1.05	1.15	1.35	0.02	0.05	0.10	0.15
		5 mm.	0.16	0.22	0.28	0.50	0.03	0.10	0.20	0.32
		10 mm.	0.05	0.14	0.16	0.16	0.04	0.15	0.24	0.42

* $\frac{1}{4}$ -inch ball test on 10 mm. thickness (i.e., approx. British standard hardness number).

readings by the other tests for any given thickness, it is possible to calculate the thickness-sensitivities of the various forms of test for any of the rubbers at any thickness within the range tested. For convenience the calculations have been limited to four rubbers, namely, B, D, F, and J, respectively very hard, medium hard, medium soft, and very soft, and to three thicknesses: 2, 5, and 10 mm. as these give an adequate comparison of the various instruments and indentors.

Results are given in Table 1; an increase in thickness produces a decrease in apparent modulus, and *vice versa*. The second decimal figure is not regarded as exact.

Table 1 shows that (1) the softer the rubber, other things being equal, the greater is the thickness-sensitivity; the two apparent exceptions (rubber D in 0.075-inch ball test on 5 and 10 mm. and Cussons Durometer on 10 mm.) are doubtless due to inaccuracies of measurement; (2) the thinner the rubber, other things being equal, the greater is the thickness-sensitivity; (3) the Shore Durometer always gives the smallest thickness-sensitivity, the 0.075-inch ball test usually giving the next smallest value, always much smaller than the $\frac{1}{4}$ -inch ball; the cone generally resembles the latter; the Rubbermeter and Cussons Durometer may give lower or higher values than the $\frac{1}{4}$ -inch ball according to the hardness and thickness of the rubber.

To obtain a rough comparison of the different tests, the 12 values of thickness-sensitivity for each have been averaged:

Shore Durometer	0.19
0.075-inch ball test	0.27
Cone test	0.50
Rubbermeter	0.52
$\frac{1}{4}$ -inch ball test	0.55
Cussons Durometer	0.58

The 0.075-inch ball test is affected by thickness variations only to about half the extent of the $\frac{1}{4}$ -inch ball test, and approaches the Shore Durometer in insensitiveness to such variations. Table 1 indicates also that by substituting the 0.075-inch ball for the $\frac{1}{4}$ -inch ball, with appropriate reduction of the loads, the test can be made on rubbers of only half the thickness without increasing the thickness-sensitivity, thus extending the useful range of the test.

These results confirm the previous conclusion¹, that reducing the size of the ball, with simultaneous reduction of the load to keep the depth of indentation the same, lessens the sensitiveness of the test to variations in the thickness of the rubber.

MODULUS-SENSITIVITY WITH DIFFERENT INSTRUMENTS, INDENTORS, AND THICKNESSES OF RUBBER

Modulus-sensitivity may be defined as the difference in hardness number produced by 1 per cent variation in the modulus of the rubber. Values for modulus-sensitivity are included in Table 1.

These data show that: (1) modulus-sensitivity is nearly always greater the softer the rubber, other things being equal; the only exception is the Cussons Durometer, where there is a decrease on passing to the softest rubber (J); (2) the thinner the rubber, other things being equal, the smaller is the modulus-sensitivity, with one exception (J, Cussons Durometer, 10 mm.); (3) with only one apparent exception (D, $\frac{1}{4}$ -inch ball test on 10 mm.) the 0.075-inch ball test gives the highest modulus-sensitivity throughout, the $\frac{1}{4}$ -inch ball test being usually the next in order, the cone test next; among the three remaining instru-

ments the order of merit varies according to the rubber and thickness, and (4) the Shore and Cussons Durometers give the most uniform values over the range of thicknesses and hardnesses examined; the Rubbermeter shows the greatest variation, and is extremely insensitive on the harder rubbers.

To obtain a rough comparison of the different tests, the twelve values of modulus-sensitivity for each have been averaged (see Table 2). As the size of one scale unit varies from one instrument to another, an alternative comparison is obtained by expressing modulus-sensitivity as the linear movement of the end of the pointer per 1 per cent difference in modulus (see Table 2).

TABLE 2

Test	Average modulus-sensitivity (scale units)	Length of one unit (inch)	Average modulus-sensitivity (inch)
0.075-inch ball test	0.55	0.055	0.030
$\frac{1}{4}$ -inch ball test	0.43	0.055	0.024
Cone test	0.28	0.055	0.015
Rubbermeter	0.15	0.041	0.0062
Shore Durometer	0.21	0.017	0.0036
Cussons Durometer	0.21	0.015	0.0032

The greater sensitivity of the tests with ball indentors, especially the smaller ball, is very striking when considered in terms of the movement of the pointer. The two Durometers have very low sensitivity.

The modulus-sensitivity figures in Table 1 belie the widely held view that indentation hardness tests on thin rubber specimens are unsatisfactory because the reading is so much affected by the rigid underlying surface that it is insensitive to variation in the hardness of the rubber. The tests are certainly less sensitive on thin than on thick samples, but not so much so as to make them of doubtful value. Even on 2 mm. thickness the modulus-sensitivity never falls below about two-thirds of the value for a 10 mm. thickness of rubber B, except with the Rubbermeter. Indeed, on the softer rubbers F and J the modulus-sensitivity on 2 mm. is greater than on a 10 mm. thickness of B. Hence there is no logical ground for the view that tests on samples as thin as 2 mm. give unsatisfactory results.

The 0.075-inch ball test gives relatively high modulus-sensitivity on 2 mm. thickness, and so is particularly advantageous for thin samples and could be used on thicknesses even less than 2 mm. without undue loss of modulus-sensitivity.

When thin samples are used, small variations in thickness have a greater effect on the hardness number; hence there is a greater need for minimizing thickness variations or correcting for these. This point is discussed more fully in the following section.

THICKNESS TOLERANCES FOR SPECIFICATION AND OTHER TESTS

As the hardness number depends on the thickness of the sample, a hardness test for specification purposes must define thickness limits, unless the readings are to be corrected to a standard thickness. The latter can be done by the curves shown in Figures 1 to 6, but the former proceeding will probably be preferred in most cases. It becomes necessary, therefore, to decide what thickness variation is permissible in a rubber of any given hardness and nominal thickness so that the errors due to this variation shall be within predetermined limits.

Strictly speaking, the conditions should be designed to give a predetermined accuracy to the measurement of the elastic modulus, which is the real object of the test. The permissible thickness variation in this case is easily determined from the thickness-sensitivity data in Table 1 (for intermediate thicknesses and hardnesses the values of thickness-sensitivity can be determined by interpolation). If it is required to determine the permissible thickness variation for a given accuracy expressed in scale units, this is readily deduced from the thickness/hardness number curves in Figures 1 to 6.

As a general rule, the thinner or the softer the rubber, the less is the permissible percentage variation in thickness for a given accuracy of hardness measurement.

SUMMARY

Charts are given which enable readings on the R.A.B.R.M. gauge ($\frac{1}{4}$ -inch ball, 0.075-inch ball, and conical indentor), Shore Durometer, Cussons Durometer, and Rubbermeter to be converted from any thickness of rubber to any other thickness, within the range 1.7 to 12.6 mm. The chart for the R.A.B.R.M. gauge, $\frac{1}{4}$ -inch ball, would be approximately correct for Pusey-Jones Plastometer readings, and that for the R.A.B.R.M. gauge, 0.075-inch ball, approximately correct for the British Standard hardness number⁶.

The curve relating the readings of one gauge to those of another varies with the thickness of the rubber, and the data given enable correlation curves to be constructed for any required thickness.

The extent to which the measurement of hardness is affected by thickness variation is expressed as the thickness-sensitivity, and values of this quantity for each form of test are tabulated for rubbers of various hardnesses and thicknesses. These results confirm the advantages previously observed¹, as regards insensitiveness to thickness variations, of reducing the size of the ball with simultaneous reduction of the load to keep the indentation the same, as has since been done in the British Standard hardness test⁶.

The sensitiveness of the hardness reading to small changes in the true hardness (elastic modulus) of the rubber is expressed as modulus-sensitivity, values of which are tabulated for each form of test and for various rubbers and thicknesses. The 0.075-inch ball test is the most sensitive, especially on small thicknesses. Attention is drawn to the comparative insensitiveness of the Shore and Cussons Durometers and to the extreme insensitiveness of the Rubbermeter on fairly hard rubbers.

There is no ground for the common belief that hardness tests on thin rubber samples are unsatisfactory. With reasonable care they can be made as reliable and informative as tests on thick samples. This fact should lead to hardness tests being used in many cases where they have hitherto been considered inapplicable.

The results of this investigation largely eliminate an unknown variable hitherto inherent in hardness test results, namely, the effect of the thickness of the rubber. The ideal way of expressing such results would be to give the readings on an infinite thickness. This infinity value, however, cannot be deduced accurately from the present thickness/hardness number curves owing to the uncertain extrapolation involved. Indeed, in view of the large thickness required to approach the infinity value on the softer rubbers, and the consequent difficulty of ensuring sufficiently uniform vulcanization, the experimental determination of the infinity value might not be a simple matter. It seems best, therefore, to adopt a standard thickness for expressing hardness figures.

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X. CHOICE OF SIZE AND FORM OF BALL INDENTOR

J. R. SCOTT

INTRODUCTION

Previous work on the ball indentation hardness test¹, has shown that, by reducing the size of the ball, with simultaneous reduction of the indenting force to keep the depth of indentation about the same, the sensitiveness of the test to variations in the thickness of the rubber can be reduced. On the other hand, if the ball size is reduced too much it is impossible to make the readings on all rubbers agree with those of the former standard test using the $\frac{1}{4}$ -inch ball and 1-kg. load, because above a certain limit (limiting indentation) the readings with the small ball are abnormally high.

With the $\frac{1}{4}$ -inch ball, on rubbers within the normal hardness range, the indentation (H) is related to the indenting force (F), radius of ball (R), and Young's modulus of the rubber (M) by the equation:

$$H = KR^{-0.48}(F/M)^{0.74} \quad (1)$$

where K is a constant². The existence of a limiting indentation with the smaller ball means that, above this limit, Equation (1) no longer holds.

Values of the limiting indentation determined for 0.075-inch and 0.04-inch diameter balls¹ showed it to be roughly proportional to the diameter of the ball. The present experiments have been made to determine more exactly the limiting indentation and its relationship to ball size, since this matter has an important bearing on the choice of the size of ball for hardness tests.

DETERMINATION OF THE LIMITING INDENTATION

The first experiments were made with a ball indenter 0.075-inch (1.91 mm.) in diameter, in the form of a cylindrical plunger of this diameter with a hemispherical end. Tests were made with the R.A.B.R.M. hardness gauge³, the hardness number being measured as the difference between the depths of indentation by loads of 22 and 488 grams, these loads were calculated to give a differential reading equal to that of the $\frac{1}{4}$ -inch ball with 1-kg. load. Readings were taken in this way, and also with the $\frac{1}{4}$ -inch ball and 1-kg. load, on several very soft vulcanized rubber samples, about 1 cm. thick (see Table 1).

The two sets of readings agree closely up to about 140, beyond which the 0.075-inch ball readings rapidly rise above the others. Plotting the two series of figures one against the other (curve A, Figure 1) shows that the agreement ceases at a reading of 138. With the 0.075-inch ball, the total indentation corresponding to this differential reading of 138 is 156, *i.e.*, 1.56 mm., which is therefore the limiting indentation for this ball.

TABLE 1
HARDNESS NUMBER (DEPTH OF INDENTATION, MM/100)

Rubber	$\frac{1}{8}$ -inch ball	0.075-inch ball
A	88 $\frac{1}{2}$	88 $\frac{1}{2}$
B	130	130
C	140	141
D	149	157
E	158	172
F	171 $\frac{1}{2}$	200
G	176 $\frac{1}{2}$	211
H	207	285

TABLE 1A
HARDNESS NUMBER (MM./100)

Rubber	$\frac{1}{8}$ -inch ball	0.075-inch ball
B	136	133
C	147 $\frac{1}{2}$	144 $\frac{1}{2}$
D	157	163
E	165	177

The limiting indentation is not greatly influenced by increasing the thickness of the rubber. This was shown by repeating some of the tests, using a thickness of 15 mm.

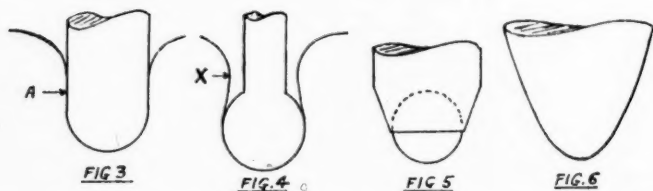
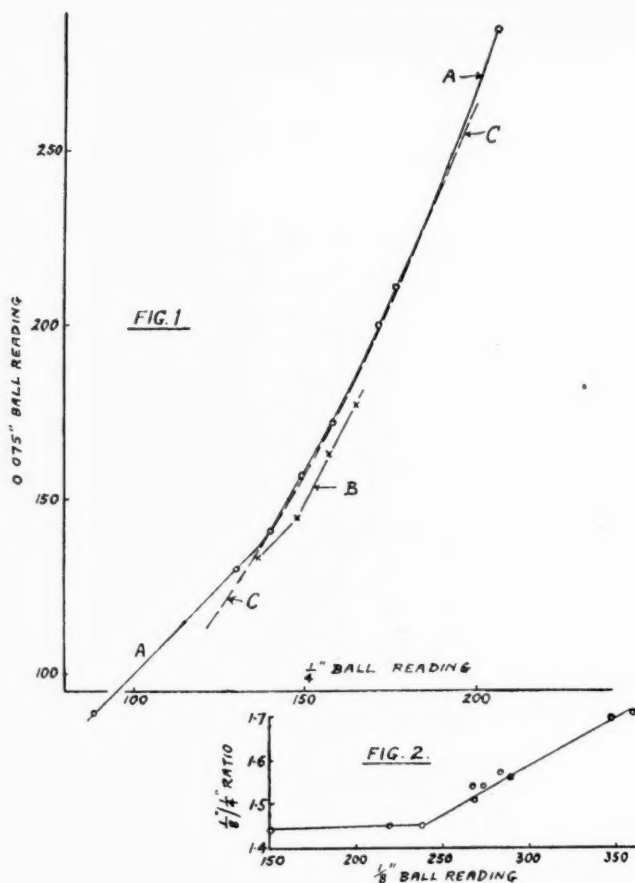
Here the small ball gives initially rather lower results than the $\frac{1}{8}$ -inch ball, because the increase in thickness has less effect with the former. The discontinuity in the curve (curve B of Figure 1) is at a reading of 147 (0.075-inch ball), corresponding to a total indentation of 1.65 mm.

In the second series of experiments, using an $\frac{1}{8}$ -inch ball, a different method was used. On relatively thick (say 1 cm.) rubbers the ratio between the readings of the $\frac{1}{8}$ - and $\frac{1}{4}$ -inch balls under 1-kg. load is practically constant for all rubbers within the usual hardness range², because within this range, both balls obey Equation (1). If tests are made on progressively softer rubbers, the ratio remains constant until the limiting indentation of the smaller ball is exceeded, when the ratio should increase, because the readings with this ball will be higher than those corresponding to Equation (1).

In these tests (Table 2) a load of 1250 grams was used to obtain the necessary depth of indentation with the rubbers available; this change does not affect the validity of the test, because increasing the load is equivalent to an apparent reduction of the elastic modulus of the rubber. The rubbers were 1 cm. thick.

TABLE 2

Rubber	Indentation (mm./100)		$\frac{1}{4}/\frac{1}{8}$ ratio
	$\frac{1}{8}$ -inch ball	$\frac{1}{4}$ -inch ball	
A	104	150	1.44
B	150 $\frac{1}{2}$	219	1.45
C	164 $\frac{1}{2}$	238	1.45
D	173	267	1.54
J	177 $\frac{1}{2}$	268	1.51
K	177	273	1.54
L	181	283	1.57
E	185	289	1.56
F	204	347	1.70
G	210	360	1.71
H	247	>420	>1.7



Plotting the $\frac{1}{8}/\frac{1}{4}$ ratio against the $\frac{1}{8}$ -inch ball reading (Figure 2), shows that the ratio begins to increase at an indentation of about 240, *i.e.*, 2.4 mm., which is therefore the limiting indentation for the $\frac{1}{8}$ -inch ball.

Table 3 shows that the limiting indentation is approximately 0.80 times the diameter of the ball.

CHOICE OF SIZE OF BALL

The use of a small ball is advantageous to reduce the sensitiveness of the test to variations in the thickness of the rubber¹. In drafting the British Stand-

TABLE 3

Ball diameter (<i>D</i>)	Limiting indentation (mm.) (<i>L</i>)	<i>L/D</i>	Reference
1 mm.	c. 0.7	c. 0.70	4
0.075-in. (1.91 mm.)	1.6	0.84	4
0.075-in. (1.91 mm.)	1.56	0.82	present tests
0.075-in. (1.91 mm.)	1.65	0.86	1 cm. thickness present tests
$\frac{1}{8}$ -in. (3.18 mm.)	2.40	0.76	1.5 cm. thickness present tests

ard hardness test⁵, it was agreed that this should give readings approximately equal to those of the former $\frac{1}{8}$ -inch ball test, with 1-kg. load, on all rubbers normally encountered, *i.e.*, up to a hardness number of about 170, and that hardness number should be determined as the difference between the indentations under a small zero load and a much larger total load. It is shown below⁶ that the optimum zero load is about 5 per cent of the total load, and the corresponding total indentation 1.11 times the differential reading; thus a hardness number of 170 corresponds to a total indentation of 189, *i.e.*, 1.89 mm.

The ball selected should therefore have a limiting indentation of at least 1.89 mm., and since this indentation is 0.80 times the ball diameter the latter must be at least 2.36 mm. A $\frac{3}{32}$ -inch (2.38 mm.) ball is therefore suitable. This has the further advantages of being the standard adopted by the American Society for Testing Materials⁷ and of being readily obtainable in the form of balls as used for bearings.

From Equation (1) suitable loads for the $\frac{3}{32}$ -inch ball, to give a differential reading equal to that for the $\frac{1}{8}$ -inch ball with 1-kg. load, are found to be: zero load, 30 grams; total load 575 grams. Later experiments⁸ showed that 565-gram total load was preferable.

INDENTATION BY A BALL BEYOND THE LIMITING INDENTATION

The above results show that when the indentation exceeds 0.80 of the ball diameter, Equation (1), characteristic of indentation by a ball, no longer holds.

With a ball carried on a stem nowhere larger in diameter than the ball itself, it would be expected that when the indentation is relatively deep the behavior would become more like that of a cylindrical plunger. Previous results¹ show that for a flat-ended plunger:

$$H = KF/M \quad (2)$$

where *K* is a constant which depends on the diameter of the plunger.

If it is assumed that above the limiting indentation the ball indenter behaves like such a plunger, Equation (2) gives the theoretical form of the curve for, say, the 0.075-inch ball reading plotted against the $\frac{1}{8}$ -inch ball reading above the limiting indentation of the former. Such a curve is shown by *C* in Figure 1; the close agreement with the experimental curve (*A*) shows the above assumption to be substantially correct.

A few observations were made on the shape of the indentation produced during the hardness test, by using a block of transparent vulcanized rubber, through the side of which the indentation could be observed.

When a cylindrical indenter with a hemispherical end is pressed into the rubber to a depth somewhat greater than its diameter (Figure 3), the rubber touches the cylindrical surface of the indenter, as shown at *A*; that is, a part of

the indentation is bounded by a cylindrical surface. With a ball fixed to a stem of small diameter (Figure 4), the wall of the indentation bulges inwards, as shown at X, when the indentation substantially exceeds the ball diameter.

The formation of a cylindrical part in the bounding surface begins at an indentation about 0.8 of the diameter of the indenter, that is, approximately at the limiting indentation. It would thus appear that the latter is the indentation at which this cylindrical part begins to form. According to this view, Equation (1) is that characteristic of the formation of a substantially part-spherical indentation; when this has increased to a complete hemisphere, and the formation of a cylindrical part begins, the Equation (2) characteristic of indentation by a plunger takes its place.

FORM OF INDENTOR

Ball indentors are sometimes made by fixing a ball (*e.g.*, as used for ball bearings) in a mounting, as shown in Figure 5. This would behave differently from that shown in Figure 3 if the indentation were deep, as the rubber would not be able to close in to such an extent around the upper part of the indenter. Thus, greater resistance would be offered to penetration, and the indentation under a given load would be reduced. By suitably shaping the mounting it might be possible to counteract the tendency of the indentors shown in Figures 3 and 4 to deviate from the characteristic ball Equation (1) by giving too high readings above the limiting indentation. Alternatively, a paraboloidal indenter (Figure 6) might serve this purpose.

SUMMARY

When the depth of the indentation produced by a ball, fixed on a stem nowhere greater in diameter than the ball itself, exceeds 0.8 of the ball diameter, the character of the test changes and the indenter behaves very much like a cylindrical plunger, *i.e.*, the indentation increases more rapidly, with increasing softness of the rubber or increasing load, than is the case with a normal ball indentation.

It follows that a small ball, such as has been recommended for reducing the influence of the thickness of the rubber¹, does not give results equal to those with the former standard $\frac{1}{4}$ -inch ball and 1000-gram load, if the indentation exceeds 0.8 of the small-ball diameter. This sets a limit to the extent by which this diameter can be reduced (to minimize thickness effects) while retaining agreement with the readings of the $\frac{1}{4}$ -inch ball test. It is concluded that $\frac{3}{32}$ -inch is the most suitable diameter for the indenting ball; this has been adopted in the British Standard Methods of Testing Vulcanized Rubber⁵.

When a ball is fixed in a mounting of larger diameter than the ball itself, the hardness reading may be reduced when the indentation is relatively deep. This effect or the use of a paraboloidal indenter might be utilized to avoid the abnormally high readings otherwise given by a ball when the indentation exceeds 0.8 of its diameter.

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XI. INFLUENCE OF GAUGE-SPRING PRESSURE AND FRICTION IN THE INDENTATION HARDNESS TEST

J. R. SCOTT

Attention has already been drawn¹ to the advantages of using a differential method in ball indentation hardness tests, *i.e.*, taking the hardness reading as the difference between the depths of the indentations produced by a small zero load and by a much larger total load, and this method has been adopted as the British Standard procedure².

When an initial reading under a small zero load is taken, however, errors introduced by residual spring pressure or by friction in the dial micrometer gauge may be much more serious. Residual spring pressure is the resultant force on the indenter due to the spring which, in most gauges, actuates the gauge stem and to the weight of any platform or other fitting attached to the stem. This force may be either upwards or downwards, according to circumstances. In an ideal gauge, residual spring pressure and friction would be absent, but in practice they are often present. Thus, if the gauge contains a spring, the tension in this varies according to the position of the stem, so that the residual spring pressure varies with the depth of indentation, and therefore cannot always be zero. The effect of this variation is to reduce the effective load on the indenter as the depth of indentation increases.

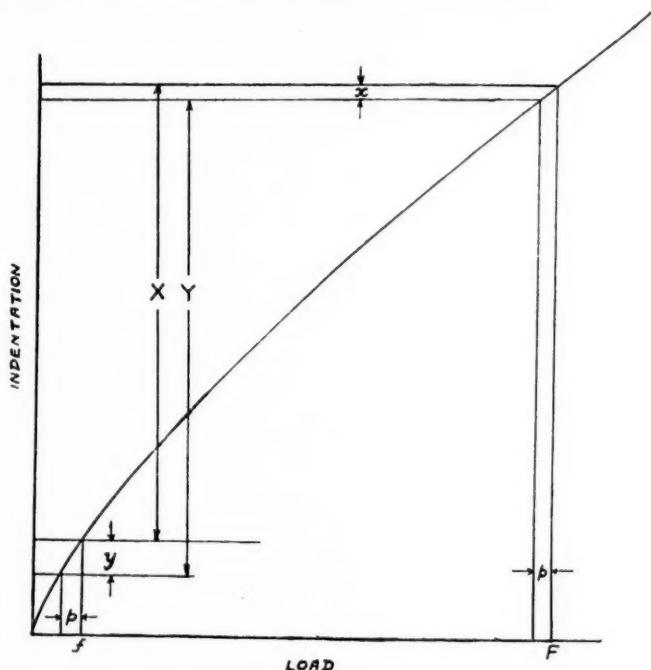


Fig. 7.

The effect of a small residual spring pressure or friction (these are termed collectively load error) on the hardness reading is seen from Figure 7, showing the curve relating indenting force and indentation for a ball¹. With a large force F a small load error p (in this case negative) produces only a small error (x) in the indentation, but with a small force f the error is much greater (y).

If f and F are the zero and total loads respectively in a differential hardness measurement, the result (difference between the two indentations) will be increased from X to Y by the load error p . Moreover, the smaller the zero load f , the greater is the resultant error in the hardness reading, other things being equal.

In considering the effect quantitatively, forces acting downwards are considered as positive and those acting upwards as negative.

Let

f = zero load

F = total load

p = load error, = $P + VI$, where P is the value at zero indentation, and V is the change per unit change in the indentation I ; V is always negative

h = true zero indentation under load f

$h + dh$ = false zero indentation under load ($f + p$)

H = true total indentation under load F

$H + dH$ = false total indentation under load ($F + p$)

If dh and dH are very small, p may be taken to have the values $(P + Vh)$ and $(P + VH)$ at indentations $(h + dh)$ and $(H + dH)$, respectively.

With a given rubber and ball indenter, it follows from the known force/indentation relationship¹ that:

$$h = Kf^{0.74} \quad (i)$$

$$h + dh = K(f + P + Vh)^{0.74} \quad (ii)$$

$$H = KF^{0.74} \quad (iii)$$

$$H + dH = K(F + P + VH)^{0.74} \quad (iv)$$

where K is a constant.

The error (dR), introduced into the differential hardness reading ($H - h$) by the load error, equals $(dH - dh)$, which from Equations (i) to (iv) equals

$$K[f^{0.74} - (f + P + Vh)^{0.74} - F^{0.74} + (F + P + VH)^{0.74}]$$

Expanding the terms in brackets by the binomial theorem, and neglecting squares and higher powers of P and V (assumed to be small compared with f and F), gives:

$$0.74 KP(F^{-0.26} - f^{-0.26}) + 0.74 KV(HF^{-0.26} - hf^{-0.26})$$

It is more logical to consider this error as a percentage of the true hardness reading ($H - h$). Evaluating H and h from Equations (i) and (iii), and putting f equal to zF , the percentage error is:

$$dR, \% = \frac{74P(1 - z^{-0.26}) + 74KVF^{0.74}(1 - z^{0.48})}{F(1 - z^{0.74})} \quad (v)$$

This equation shows that the error is greater the smaller the total indenting force (F), other things being equal. It shows also that dR is zero if the top line of the right-hand expression is zero; since $KF^{0.74}$ equals H , this condition is satisfied if:

$$P(1 - z^{0.26}) + VH(1 - z^{0.48}) = 0 \quad (\text{vi})$$

This shows that the conditions can be adjusted so that no error in the differential hardness reading arises from the load error or from the variation of the spring pressure with the position of the gauge stem. However, this adjustment can be correct only for one value of H , and therefore would have to be varied for each rubber. Moreover, in practice P may vary unsuspectingly owing to the development of friction, and both P and V may change owing to alteration of the spring tension with time. It is, therefore, necessary to know the effects of variations in H , P , and V in an instrument nominally adjusted to give zero error.

The percentage error in the hardness reading due to a change (dP) in P (V and H being constant) is:

$$\frac{74dP(1 - z^{0.26})}{F(1 - z^{0.74})} \quad (\text{vii})$$

The effect of a change dV (H and P being constant) is:

$$\frac{74dV \cdot H(1 - z^{0.48})}{F(1 - z^{0.74})} \quad (\text{viii})$$

A change dH (P and V being constant) gives an expression analogous to (viii).

The corresponding expressions for the errors introduced into the hardness reading obtained by the direct method, *i.e.*, without the initial reading under a zero load, are obtained by omitting all the z terms in (vii) and (viii).

Table 1 gives the percentage error in the hardness reading, for various values

TABLE 1

Per cent error in hardness reading due to

z	1-gram increase in P (Formula vii)	1-gram/mm. increase in V (Formula viii)	1-mm. increase in H
0.01	-0.305	$0.120 \times H$	$0.120 \times V$
0.02	-0.235	$0.116 \times H$	$0.116 \times V$
0.03	-0.197	$0.114 \times H$	$0.114 \times V$
0.04	-0.181	$0.113 \times H$	$0.113 \times V$
0.05	-0.168	$0.112 \times H$	$0.112 \times V$
0.07	-0.149	$0.110 \times H$	$0.110 \times V$
0.10	-0.126	$0.108 \times H$	$0.108 \times V$
Direct reading without zero load	0.129	$0.129 \times H$	$0.129 \times V$

Notes.—(a) An increase in P means a numerical increase in a downward pressure or numerical decrease in an upward pressure. The effect of either is to reduce the differential hardness reading but to increase the direct reading.

(b) Since V is always negative, an increase denotes a reduction of the numerical value, which causes an increase in the hardness reading. For the same reason the effect of increasing H (last column) is to introduce a negative error.

of z , due to variations in P , V , and H ; F is taken as 575 grams³. In calculating the figures for the differential method, it is assumed that friction represents a force acting in the same direction in both zero and final readings; this is normally the case, since friction always tends to reduce the effective load. All values, unless otherwise marked, are positive.

Table 1 shows that the errors due to variations in V and H do not depend greatly on the value of z . To make the differential test as little affected by variation in P as the direct test, however, z must be at least 0.10. However, too high a value for z is undesirable because a high z means a greater total indentation for a given differential reading; typical figures for a differential reading of 100 are:

z	0	0.01	0.02	0.03	0.04	0.05	0.07	0.10
Total indentation	100	103	105½	107½	109½	111	114	118

Increasing the total indentation has the following disadvantages: (1) the range of rubbers that can be tested without exceeding the limiting indentation, above which the load/indentation relationship characteristic of a ball ceases to apply³, is restricted; (2) the disturbing effect of variations in the thickness of the rubber is increased⁴. The zero load should, therefore, be as low as is compatible with a sufficiently small error due to residual spring pressure and friction. It is considered that 0.05 is a suitable value for z ; *i.e.*, the zero load equals 5 per cent of the total load. The method of B.S. 903-1940⁶ uses this value of z , and as the total load is 565 grams, this means that friction or residual spring pressure amounting to 6 grams affects the B.S. hardness reading by only 1 per cent.

Putting z equal to 0.05 in Equation (vi) gives, as the condition for zero error: $P = 0.65 VH$. By definition p equals $(P + VI)$, and hence equals $(0.65 VH + VI)$. Consequently, if I equals $-0.65H$, p is zero.

This means that if the load error p is adjusted to zero when the position of the gauge stem corresponds to an indentation (I) of $-0.65H$, the errors in the hardness reading due to p and its variation with the position of the gauge stem is eliminated. As, however, this adjustment varies with the value of H ; hence according to the rubber under test, a single adjustment does not suit all rubbers. For practical purposes, however, an average value of 0.75 mm. may be adopted for H ; the load error p should, therefore, be adjusted to zero when the tip of the indenting ball is 0.5 mm. (*i.e.*, 0.65×0.75) above the surface of the rubber.

SUMMARY

A discussion is given of the effects of the spring which, in many dial micrometer gauges, applies a small upward or downward force to the gauge stem, and of the effects of friction in the gauge.

When hardness tests are made by the differential method, the reading being taken as the difference between the indentations produced by a small zero load and a much larger total load, the errors introduced by unbalanced gauge spring pressure and by friction may be much more serious than when a direct hardness reading, *i.e.*, without an initial zero load, is taken.

Other things being equal, the resulting percentage error in the hardness reading is greater the smaller indenting load. This is a further reason, additional to that already advanced³, for limiting the reduction of ball size and load which has been advocated to reduce the influence of the thickness of the rubber.

If the gauge contains a spring, or if friction is present, it is not possible to adjust conditions so as to eliminate the resulting errors in the differential readings on all rubbers. The errors can, however, be minimized in the following ways.

(1) By increasing the ratio (z) of zero load to total load. An excessive zero load, however, is undesirable for other reasons; a value of 0.05 for z is a suitable compromise.

(2) By adjusting the unbalanced spring pressure to zero when the gauge stem is in a certain position which depends on the value of z and the hardness of the rubber under test. Taking z as 0.05 and the average B.S. hardness number of normal rubbers as 75 (*i.e.*, an indentation of about 0.75 mm.), this position is that in which the tip of the indenting ball is 0.5 mm. above the surface of the rubber.

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XII. COMPARISON OF TESTS USING A $\frac{1}{4}$ -INCH BALL AND A $\frac{3}{32}$ -INCH BALL

J. R. SCOTT

INTRODUCTION

It was previously shown¹ that the most suitable diameter for the ball for use in hardness tests is $\frac{3}{32}$ -inch, and it was calculated that to obtain readings similar to those given by the former standard test with $\frac{1}{4}$ -inch ball and 1-kg. load, the $\frac{3}{32}$ -inch ball should be used with loads of 30 and 575 grams, the hardness number being the difference between the indentations under these loads.

EXPERIMENTAL

It is important that there should be no doubt as to the relationship between the results with the $\frac{3}{32}$ -inch ball and those given by the older $\frac{1}{4}$ -inch ball test. Hardness measurements were therefore made by both methods on several rubbers, and as a result of this work, the total load was reduced from 575 to 565 grams, as this was found to give better agreement with the values obtained by the $\frac{1}{4}$ -inch ball test.

Most of the rubbers used were not specially made for these tests, but were selected at random from a large variety of rubbers made for other purposes. Usually five samples from each mix, vulcanized for different periods, were available, the optimum vulcanization being generally somewhere between the 3rd and 5th of the series; in most cases the first vulcanizate was definitely undervulcanized.

Two types of rubber specimens were examined: (1) Vulcanized as sheets 2.5 mm. thick; for the hardness tests two pieces measuring 25×35 mm. were superposed, giving a total thickness of 5 mm.; (2) Vulcanized as sheets 5 mm. thick; two discs 45 mm. in diameter were superposed to give a thickness of 10 mm. All the specimens were conditioned for 24 hours at 20° C before being tested.

The tests were made with an R.A.B.R.M. hardness gauge². For the $\frac{3}{32}$ -inch ball tests, the weight of the loading platform was adjusted so as to balance the

gauge spring when the tip of the indenting ball was 0.5 mm. above the plane of the gauge foot, as previously recommended³.

The two methods of test were as follows.

(1) $\frac{1}{4}$ -inch ball test.—A load of 1 kilogram was applied for 30 seconds, during which the table was gently tapped to overcome friction. In this method a difficulty arises with very hard rubbers, because the gauge is not heavy enough to press the surface of the rubber into conformity with the gauge foot, and this may cause an error owing to the surface of the sample, at the point immediately under the indenter, not being in the plane of the foot. An approximate correction can usually be obtained by gently depressing the gauge stem, before applying the load, until the ball just touches the rubber, taking a reading on the gauge, and subtracting it from the final reading; this correction was applied to all the rubbers with hardness numbers below 40.

(2) $\frac{3}{32}$ -inch ball test.—A load of 30 grams was applied for 5 seconds and a reading taken; an additional load of 545 grams (or 535 grams) was then applied for 30 seconds and a further reading taken, the difference between the readings being the hardness number. The table was tapped, as in method (1), during the application of both loads.

RESULTS

In each test four readings, two on each side of the specimen, were taken and averaged. The results of the comparative tests using 575 grams total load with the $\frac{3}{32}$ -inch ball are given in Table 1.

The $\frac{3}{32}$ -inch ball test usually gives the higher reading. This is particularly noticeable with rubbers vulcanized for the shortest period, for which the difference is generally larger than on more fully vulcanized samples of similar hardness. Such an effect would be expected from the observation⁴ that the creep shown by undervulcanized rubbers in hardness tests is somewhat accentuated by the use of the smaller ball, though scarcely to an extent sufficient to account for some of the large differences now found between the results of the two tests. As such undervulcanized rubbers are of little technical importance, it is justifiable to exclude them and so obtain an estimate of the difference that would be encountered in normal testing work.

On both thicknesses of rubber the difference between the $\frac{3}{32}$ - and $\frac{1}{4}$ -inch ball readings increases with the hardness number. To show this more clearly, the difference was plotted against hardness number; values of the difference corresponding to various hardness numbers, read off from a smoothed curve, are given in Table 2. (Column 1 = 5 mm. thick samples; column 2 = 10 mm. thick samples; although figures are given to one place of decimals, they are not to be regarded as accurate to 0.1 unit.)

The differences are larger on the 5-mm. samples (column 1) than on the 10-mm. samples (column 2). This would be expected, because the $\frac{3}{32}$ - and $\frac{1}{4}$ -inch ball tests are intended to give the same results on 10 mm. thickness, and the reduction in hardness number on reducing the thickness is less with the smaller ball. From the data for variation of hardness number with thickness⁵, it is possible to estimate by how much the readings with the two balls should differ on 5 mm. thickness, assuming they give the same results on 10 mm. This difference is shown in column 3; subtracting it from the observed difference (column 1) gives a corrected difference (column 4), which is now much nearer

TABLE 1
HARDNESS NUMBERS (MM./100)

Upper figure of each pair = $\frac{1}{4}$ -inch ball reading; lower figure = difference, *i.e.*, $\frac{3}{32}$ -inch ball reading (575 grams total load) minus the $\frac{1}{4}$ -inch ball reading.

Vulcaniza- tion (b)	Specimens 5 mm. thick					Specimens 10 mm. thick				
	1	2	3	4	5	1	2	3	4	5
Mix No.										
1398B	15 0	13 2	13 3	13 3	15 3	43 2	36 -1	32 1	32 -2	31 2
1398A	26 4	29 -1	23 1	26 0	26 -1	66 1	63 -1	58 0	54 -2	55 0
1398C	27 0	25 1	29 -2	26 2	24 3	73 -1	64 1	59 0	59 -2	54 0
1398A	32 3	29 0	25 4	24 4	28 1	96 4	86 2	80 5	88 2	87 2
1398D	51 1	42 1	43 4	42 0	43 -1	128 10	110 5	98 6	102 4	92 5
1399A	(a) —	84 9	78 6	72 7	77 5	137 4	129 2	128 4	129 4	131 3
1399C	(a) —	83 8	81 7	76 6	75 8	147 11	139 6	130 2	127 3	136 3
1404E	83 2	80 4	80 5	81 4	80 5	161 14	147 3	136 3	137 5	137 6
1399B	94 13	77 8	80 6	79 5	— —	162 8	136 4	136 4	137 4	144 3
1410B	114 24	94 11	86 10	81 7	84 8	142 9	138 5	138 4	138 5	141 8
1410A	117 23	97 11	85 11	85 8	85 6	162 9	148 7	143 6	137 6	139 5
1404F	94 9	91 10	88 11	87 10	87 8	173 13	165 13	165 8	140 5	140 5

(a) Too undercured to test.

(b) The numbers 1-5 represent increasing vulcanization periods.

TABLE 2

Hardness No.,
 $\frac{1}{4}$ -inch ball
(=approx. B.S.
Hardness No.)

	1	2	3	4	5	6
20	1.0	—	0.6	0.4	0.4	-0.2
40	2.0	-0.5	1.5	0.5	0.0	-0.5
60	4.5	0.3	2.7	1.8	1.1	-0.5
80	7.0	1.5	4.5	2.5	2.0	0.5
100	10.5	2.5	7.5	3.0	2.8	-0.3
120	—	4.0	—	—	4.0	0.1
140	—	5.5	—	—	5.5	0.5
160	—	8.0	—	—	8.0	1.0

to that observed on the 10 mm. samples (column 2) with which it should, theoretically, be identical.

Column 5, giving the mean of the differences deduced from the 10-mm. specimens (column 2) and 5-mm. specimens (column 4), shows that the $\frac{3}{32}$ -inch ball test has usually given slightly higher results than the $\frac{1}{4}$ -inch ball test, especially on very soft rubbers. From these results it was estimated that a total load of 565 grams instead of 575 grams in the $\frac{3}{32}$ -inch ball test would give better agreement with the $\frac{1}{4}$ -inch ball results. Further tests were accordingly made on specimens 10 mm. thick, using the reduced load (see Table 3).

TABLE 3

HARDNESS NUMBERS (MM./100) ON SPECIMENS 10 MM. THICK

Upper figure of each pair = $\frac{1}{4}$ -inch ball reading; lower figure = difference, *i.e.*, $\frac{3}{32}$ -inch ball reading (565 grams total load) minus the $\frac{1}{4}$ -inch ball reading

Vulcaniza- tion Mix No.	2	3	4	5
1509C	— —	— —	18 0	17 0
1509B	— —	— —	30 1	28 1
1452A	34 -3	29 -1	28 -1	27 -1
1509D	— —	37 -1	34 -1	— —
1509A	— —	— —	40 1	39 1
1153B	71 -2	64 0	62 0	60 0
1452D	88 -1	84 0	83 0	82 0
1452C	112 0	104 -1	102 0	98 -3
1212D	126 3	124 1	122 2	121 1
1375A	140 0	134 0	131 -1	129 0
1211F	166 1	163 0	160 1	158 1

These results have been examined in the same way as those in Table 1; the values so found for the difference between the $\frac{3}{32}$ -inch and $\frac{1}{4}$ -inch ball readings are shown in Column 6 of Table 2. Comparison with column 5 shows that much better agreement between the two readings has now been obtained, the average difference for the whole set of results being only -0.05 unit. It may therefore be concluded that the $\frac{3}{32}$ -inch ball test, using 565 grams total load, gives satisfactory agreement with the $\frac{1}{4}$ -inch ball test over the whole hardness range considered.

Another important point in comparing the two forms of test, is the variation among measurements on the same rubber. This is represented by the following standard deviation: $\frac{1}{4}$ -inch ball test, 1.31 units; $\frac{3}{32}$ -inch ball test, 1.43 units. As the difference between these figures is just not statistically significant (for 130 degrees of freedom in each test) the $\frac{3}{32}$ -inch ball test is clearly under no disadvantage as regards accuracy.

SUMMARY

A comparison has been made between the results given by two forms of indentation hardness test: (1) $\frac{1}{4}$ -inch ball and 1-kg. load; (2) $\frac{3}{32}$ -inch ball with 30-gram zero load and total loads of 565 and 575 grams. It is shown that with the loads specified in the British Standard test, using the latter ball⁶, namely: 30 and 565 grams and using rubber specimens 10 mm. thick, the results obtained by the two methods agree closely on all rubbers having hardness numbers up to about 160. Both methods give equally consistent results.

The British Standard test therefore satisfies the requirement that it was intended to fulfil, namely, of giving substantially the same results as the $\frac{1}{4}$ -inch ball test on rubbers 10 mm. thick; the advantage of the smaller ball in giving readings less influenced by variations in the thickness of the rubber has already been demonstrated⁵.

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- ⁶ British Standards Institution, *Brit. Standard Methods of Testing Vulcanized Rubber*, B. S. 903-1940.

CORRELATION OF LABORATORY AND SERVICE ABRASION TESTS OF RUBBER TIRE TREADS

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In the paper entitled "Correlation of laboratory and service abrasion tests of tire treads", by A. E. Juve and F. L. Graves, an error occurs in the original publication in the May 1947 issue of the *ASTM Bulletin*, in the May 1947 issue of the *India Rubber World*, and in the April 1948 issue of RUBBER CHEMISTRY AND TECHNOLOGY.

On page 526 of the April 1948 of RUBBER CHEMISTRY AND TECHNOLOGY, the sentence itemized (d) should read: "Correlation is generally good when various grades of carbon blacks are compared."

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THE NORTHERN CALIFORNIA RUBBER GROUP

The Northern California Rubber Group was organized by about twenty-five rubber chemists meeting at the Claremont Hotel, Berkeley, on November 17, 1942. Because there are only about a dozen rubber manufacturers in Northern California, the Group probably would not have been started if it had not been for those hectic days in 1942 when rubber chemists were faced with many new problems caused by the shortage of natural rubber. None of the rubber chemists knew much about GR-S or other synthetic rubbers, and the war effort made coöperation necessary. Thus the Group was formed as a direct result of the desire of the rubber manufacturers to exchange ideas and information and to obtain further information from visiting rubber technologists.

If any individual could be said to have started the idea of forming the Group, this man was V. H. Vodra, who organized technical meetings even before the Group itself was formed.

The spirit of coöperation which brought the Group together has characterized it ever since, and in spite of the small number of rubber manufacturers in this area, the Group has grown to a membership over one hundred. Meetings are usually held the last Thursday of each month except in the summer months and in December. The activity in the summer consists of an outing at a local mountain park or beach, and in December a Christmas party, generally at The Willows in Orinda.

The regular meetings are always held in the East Bay area because of the larger number of members there, but meetings have been held elsewhere over the years. The most popular, and probably the permanent location, is the beautiful Claremont Hotel in Berkeley, overlooking San Francisco bay.

The distinguishing characteristic of the Northern California Rubber Group is the emphasis placed on the technical aspect of the rubber business. This was a logical result of the desperate conditions existing at the time of the formation of the Group. The technical nature of the Group immediately attracted all of the technical rubber men in the area, both in and out of the rubber industry itself. These men have retained their memberships, and the essence of the Group has remained technical. Because of the nature of the membership, programs of a general nature are seldom held, and the technical session is the sum and substance of the meetings.

Other outstanding characteristics of the Group are good fellowship, coöperation between members, friendliness to visitors, and the unique decision by the members that the Group shall not solicit money or prizes for meetings and outings, and shall accept only donations voluntarily offered. The Group also differs from some other rubber groups in that the meetings and membership are open to women who have an interest in rubber technology.

The Group got off to a good start in 1943 under the first chairman, H. J. Jordan. He was followed by L. C. Boller in 1944, R. D. Kettering in 1945, L. L. Shafer in 1946, G. B. Farwell in 1947 and R. E. Morris in 1948. Among the many members who have contributed much to the success of the Group are E. P. Coxhead, L. H. Dimpfl, F. Durbin, W. D. Good, R. J. Henderson, J. Kirby, J. A. Liljegren, N. McIntyre, G. I. Petelin, V. F. Sagues, F. W. Swain and W. F. Winterbourne.

An infallible source of entertainment for the Group is its own "barbershop" quartette. This musical organization is composed of W. D. Good, R. D. Kettering and F. W. Swain. The fourth member of the quartette varies between W. E. Boswell and J. A. Liljegren. Another enjoyable feature of all meetings is the current events report by J. Kirby in his inimitable style.

The Northern California Rubber Group, like all the rubber groups in this country, has done a great deal to create good will among its members and the companies which they represent. It is a recognized fact that there is a more friendly relationship between the competing rubber companies in the area than was the case before the inception of the Group.

H. J. JORDAN AND G. B. FARWELL

NEW BOOKS AND OTHER PUBLICATIONS

Nov 1947
PRACTICAL LATEX WORK. H. J. Stern. Foreword by R. J. Noble. The Blackfriars Press, Ltd., Leicester, England. Second Edition, 1947. Boards, 4 $\frac{1}{2}$ by 7 $\frac{1}{4}$ inches. 107 pages. Price 8/6d.—The first edition of Stern's very useful little book, published in 1940, filled a need of a source of information on latex and

latex processing for the plant chemist and engineer that proved to be very valuable to those in the field or about to enter it. The demand for the book continued long after the available copies were exhausted. This second English edition includes most of the material of the first edition in a revised and improved form and new material on rubber thread and sponge and on synthetic latices.

The various types of natural latices are discussed in the first chapter, as before, together with vulcanized latex and artificial dispersions. The details of equipment, compounding ingredients and the processing of the latex, the necessary pastes and emulsions, etc., are treated in the second chapter.

The third chapter is devoted to the actual manufacture of dipped goods from latex, and the fourth chapter to the application of latex to textiles, fibers, and paper. Mention is made of the Positex process for textile impregnation in this latter chapter.

The fifth chapter includes some discussions of processes involving extrusion and latex sponge, and the sixth chapter offers some information on Neoprene, GR-S, and Thiokol latices, but this latter does not cover advances since early 1947.

The book concludes with a short section on calculating the cost of latex compounds. [From the *India Rubber World*.]

COMPARING RUBBERS. J. F. McWhorter. The Ohio Rubber Co., Willoughby, Ohio. $8\frac{1}{2} \times 11$ in. 8 pp.—The material from which this pamphlet was produced first appeared in the February, 1948, issue of *Machine Design*, and presents in a concise form a comparison of typical rubbers, both natural and synthetic, now in use with respect to their properties, mechanical applications and economies in production. Engineering drawings, charts, photographs and tables are included. A supplementary section is devoted to the adhesion of rubber to metal. The comparative bonding qualities of natural and synthetic rubbers to different types of metal are discussed. [From *The Rubber Age* of New York.]

DIE MAKROMOLEKULARE CHEMIE. Volume 1, No. 1-2 (September, 1947). H. Staudinger, editor, Freiburg im Breisgau. Price, \$7.50 per volume—3 issues.—A journal of macromolecular chemistry was started in Germany in the fall of 1947. H. Staudinger, a leading authority in the field and editor of the new magazine, has succeeded in assembling a group of outstanding coeditors in Germany, Sweden, and Switzerland, whose names assure a high scientific level and a great variety of subjects. Articles covering the entire field of macromolecular chemistry will appear in German, English, and French; the journal will be published at irregular intervals, three issues constituting one volume.

Staudinger himself opens the first issue with his Communication No. 321 on macromolecular substances, which is a general survey of the field of natural and synthetic polymers.

It is certainly gratifying that polymer chemists in Germany have succeeded in initiating this periodical as a vehicle for publishing the results of their own studies and of their contributing colleagues abroad in a comprehensive manner. Issue Number 1-2 demonstrates that there is much material available to arouse interest all over the world. The Editors of *Journal of Polymer Science* extend their congratulations to Dr. Staudinger for the publication of this new periodical, and wish *Die makromolekulare Chemie* a rapid and prosperous development. [H. Mark in the *Journal of Polymer Science*.]

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